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CHEMISTRY OF ORGANOMERCURIALS IN AQUATIC SYSTEMS

George L. Baughman, et al

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CHEMISTRY OF ORGANOMERCURIALS IN AQUATIC SYSTEMS

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Dimethylmercury, methylmercuric chloride, methylmercuric hydroxide, and methylmercuric ion were not decomposed by sunlight, but phenylmercury and sulfur-bonded methylmercuric species were readily decomposed to inorganic mercury. Detailed equilibrium calculations indicate that the sulfur-bonded methylmercuric species are the predominant species in natural waters. Quantum yields for these reactions are presented along with a technique for calculating sunlight photolysis rates from laboratory data.

The report also includes a review of the chemical literature concerning the kinetics of chemical and photochemical decomposition of organomercurials.

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SECTION I

CONCLUSIONS

1. The composition of dissolved methylmercuric species in aquatic systems is dependent on the type and concentration of complexing agents present and the pH. An analytical expression is derived that gives the relative percent of the methylmercuric species as a function of concentration and pH in the presence of eight complexing agents.

2. At pH's and concentrations expected in the environment, methylmercuric ion is not the predominant methylmercuric species. Because natural systems contain much organic and inorganic sulfur, methylmercury will exist predominantly as the sulfide or thiol complex. In the absence of sulfide or thiols, the hydroxide or chloride complex would predominate.

3. Reaction of hydrogen ion with dimethylmercury and diphenylmercury gives methane and benzene, respectively, and the corresponding organomercuric salt. The reaction is first-order with respect to both hydrogen ion and organomercury concentrations. The second-order rate constant extrapolated to 25° for dimethylmercury is 7.33×10^{-5} ℓ/mole sec and 9.67×10^{-3} ℓ/mole sec for diphenylmercury. With the known rate constants and kinetic expression, the acidolysis half-lives for these compounds can be calculated at various pH's.

4. Dimethylmercury and diphenylmercury react with mercuric salts in aqueous solution to give methylmercuric and phenylmercuric salts, respectively. The reaction rate shows a strong pH dependence, increasing dramatically as the pH is decreased. At alkaline pH's and mercuric species concentrations common to the aquatic environment, this would not be a significant degradative pathway. At acidic pH's the observed rate constant is higher and the reaction may be significant. The half-lives can be calculated from mercuric salt concentrations and pH data.

5. Formation of dimethylmercury by symmetrization reactions of methylmercuric ion or methylmercuric hydroxide occurs at a rate too slow to be significant under environmental conditions.

6. Dimethylmercury in aqueous solution does not react with dissolved oxygen, hydroxide, sulfide, iodide, or albumin at a rate fast enough to be a significant pathway for degradation.

7. Evaporative loss of dimethylmercury and elemental mercury from aqueous solution may be significant for turbulent systems. Half-lives for evaporative loss can be estimated from literature data and

calculated transfer coefficients. Based on these calculations elemental mercury is lost from solution about twice as fast as dimethylmercury.

8. The low sunlight absorption rate constants for dimethylmercury, methylmercuric ion, and methylmercuric hydroxide preclude photodecomposition as a significant pathway for degradation. Neither photosensitization nor singlet oxygen effects their decomposition.

9. Diphenylmercury absorbs sunlight in aqueous solution and photolyzes with a disappearance quantum yield of 0.27. The photolysis results in carbon-mercury bond cleavage to give elemental mercury and phenyl radicals. The minimum photochemical half-life determined in sunlight experiments is 8.5 hours.

10. Dissolved phenylmercuric salts undergo photochemical decomposition with pH independent disappearance quantum yields of 0.24. The photochemical reaction results in carbon-mercury bond cleavage and formation of mercurous salts and phenyl free radicals. The experimentally determined minimum half-lives ($\sim$ 17 hours) show that photodecomposition of these compounds may be environmentally significant under certain conditions.

11. Methylmercuric thiol and methylmercuric sulfide ion complexes undergo photodecomposition in sunlight. The methylmercuric thiol complexes have quantum yields from 0.12 to 0.16 with minimum photochemical half-lives of 46 to 120 hours. Methylmercuric sulfide ion has a quantum yield of 0.65 and a minimum half-life of 0.43 hours. The major products are methane and inorganic mercury species. Although oxygen lowers the quantum yields, photochemical reaction may still be a significant degradative pathway.

SECTION II

RECOMMENDATIONS

1. Studies are needed to elucidate the rates and mechanisms of the release of dimethylmercury and elemental mercury from sediments to overlying water. Because these materials are non-ionic and have a significant vapor pressure, they may play an important role in mercury cycling through loss at the air-water interface.

2. Calculations presented here indicate that elemental mercury and dimethylmercury are likely to volatilize from the aquatic environment Because little is known about the behavior of gaseous mercury species in the atmosphere, research should be undertaken to determine the fate of these materials.

3. The chemical and physical behavior of mercury in the environment can be determined by species with which the mercury complexes. Characterization of these complexes is essential for evaluation of the chemical, physical and biological processes in the mercury cycle. Therefore, water from sediments and from the water column should be analyzed to identify the mercury species present.

4. Redox properties of natural aquatic systems should be investigated with particular emphasis on the rates and mechanisms of oxidation-reduction reactions. An understanding of these properties is required before general statements can be made about the effect of redox potentials on organomercuric or other pollutants.

5. Ligand exchange rates should be examined in detail for complexes of mercury and other heavy metals. Our literature survey indicates that some exchange reactions with ligands common to natural waters are fast enough to approach equilibrium under environmental conditions. This study should include humic acids as well as proteins and other biological ligands.

6. Concentrations of reduced sulfur species and sulfhydryl-containing organics should be measured in natural waters. These measurements should include samples of interstitial water from sediments as well as samples from the water column. Sensitive techniques for analysis of these substances should be developed because very low concentrations can have important effects upon the complexation of organomercuric and other metallic species.

7. Light absorption and light scattering characteristics of natural waters should be determined for the wavelength region 290-700

nm. In conjunction with solar radiation intensities, these data can be used to calculate the penetration of sunlight into natural waters.

8. A general mathematical model is needed for photochemical processes in natural waters. Such a model should be capable of predicting integrated photolysis rates in natural systems based on quantum yields, ultraviolet absorption spectra, solar radiation intensities, and turbulence levels.

9. Applicability of current information on sensitization and quenching of photoreactions is limited by lack of knowledge concerning the photochemical properties of natural waters. Research is needed to define the nature of the sensitization process, quantum yields, and conditions under which sensitization occurs. These studies should also attempt to identify chemical and physical properties of natural waters that indicate the presence of potential sensitizers or quenchers.

10. A mathematical model should be developed describing the aquatic mercury cycle. The model should have sufficient detail to permit determination of the relative importance of the various proposed transport processes.

SECTION III

INTRODUCTION

Although the occupational hazards of mercury have been known for many years, its environmental impact only recently became apparent. The recent interest in the environmental implications of mercury stems primarily from two incidents in widely separated countries. First, a massive case of poisoning in Japan--the Minamata Bay incident--was attributed to industrial discharge of organomercurials.[1] Secondly, declining bird populations in Sweden was blamed on the use of phenyl and methylmercurial pesticides as seed dressings.[2] Pioneering work, particularly in Sweden, has since shown that mercury accumulates in fish to concentrations much higher than that in surrounding waters and that it exists in fish predominantly in a methylated form.[3] The widespread occurrence of methylmercury compounds remained a mystery until it was shown by Jernelöv that inorganic forms could be biologically methylated in aquatic systems.[4] No direct proof exists, however, that the mercury in fish is methylated prior to uptake.[3] Several extensive reviews of the overall mercury problem are available and should be consulted for more detail.[3,5]

Tentative descriptive models similar to Figure 1 were offered in explanation of the transformations and cycling of mercury in aquatic systems.[4] The phenylmercurials were included primarily because of their widespread release into waterways as a result of their use as fungicides.

While prior research has clearly demonstrated the importance of organomercurials, few data are available concerning the mechanisms or rates of their reactions. And although some work has been done on the non-aqueous chemistry of organomercurials, very few studies were carried out in water or, in the case of photochemical reactions, in light of wavelengths characteristic of solar radiation. The lack of relevant information may partially explain the strong reliance of environmental chemists on thermodynamics to predict the aquatic chemistry of mercury and mercury compounds. The environmental literature, as a result, contains many erroneous conclusions about the forms and reactions of organomercurials as pollutants.

The present report includes an extensive background section with a discussion of pertinent equilibria and a review of the chemical and photochemical degradation reactions of mercury and mercury compounds. Because the chemical and photochemical reactions occur by different mechanisms and require different experimental techniques, they are discussed separately.

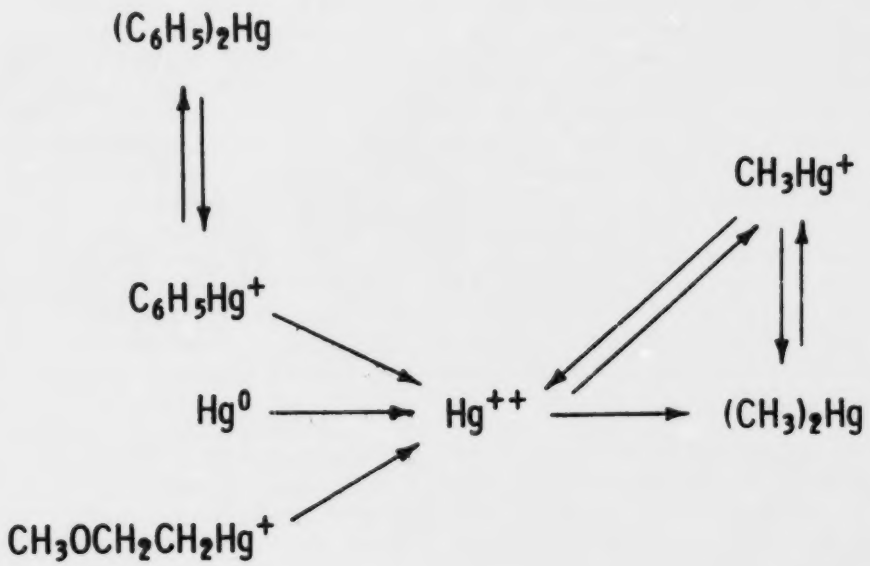
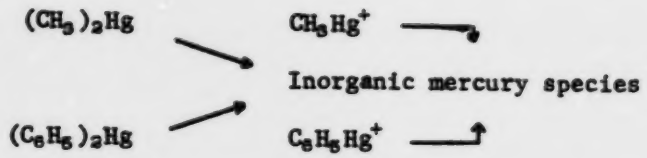


Figure 1. Model of the environmental mercury cycle.

A comprehensive kinetic study is presented of some chemical and photochemical reactions expected to result in degradation and cycling of organomercurials in the aquatic environment. Study was limited to the simple phenyl and methyl derivatives because they are known to enter aquatic systems and because higher homologs are less stable. The following reactions were studied.



The rate equations are the result of laboratory studies and should predict the rates of the respective reactions in water. They will not predict the net rate of the reaction in natural systems unless the reaction in question is the rate determining step.

SECTION IV

BACKGROUND

Chemists have long been intrigued by reactions of mercury compounds, and a vast body of literature on this subject has accumulated during the past century. Since a review of that work is well beyond the scope of this report, the interested reader is referred to several excellent books that have recently been published.[6] Also, annual reviews of mercury chemistry have been compiled since 1968 by Professor Dietmar Seyferth and his coworkers.[7-9] Bass and Makarova have recently reviewed the photochemistry of organomercurials.[10]

Since most past studies of mercury chemistry were not prompted by environmental considerations, relatively few studies were carried out under conditions that could be extrapolated to the environment. A review of the environmentally pertinent literature is presented with particular emphasis on publications related to kinetics of organomercury degradation.

EQUILIBRIA OF MERCURY REACTIONS IN WATER

Early studies of aqueous solutions of mercuric,[11] alkylmercuric,[12] and phenylmercuric[13] compounds indicated that many of these compounds react with water to form acidic solutions. Subsequent investigations[14-18] showed that reactions 1-5 account for the acid formation. The symbol X represents any electron-withdrawing ligand that forms an ionic bond with mercury, and R stands for an organic group such as methyl or phenyl. Mercury compounds with ionic Hg-X bonds are often designated as mercury "complexes" or "salts" in the literature.

$$HgX_2 \rightleftharpoons Hg^{2+} + 2X^- \quad (1)$$

$$Hg^{2+} + H_2O \rightleftharpoons HgOH^+ + H^+ \quad (2)$$

$$HgOH^+ + H_2O \rightleftharpoons Hg(OH)_2 + H^+ \quad (3)$$

$$RHgX \rightleftharpoons RHg^+ + X^- \quad (4)$$

$$RHg^+ + H_2O \rightleftharpoons RHgOH + H^+ \quad (5)$$

Although spectroscopic studies have shown that mercuric[19] and organomercuric[20] ions, like the hydrogen ion, exist as hydrated forms in water, these species will be represented for convenience as Hg^{2+}, RHg^{+}, and H^{+}, respectively.

Mercuric[21] and organomercuric[14-18] perchlorates, nitrates, and sulfates are very ionic and are thus completely dissociated in aqueous solution (eq 1 and 4). Other, less ionic mercury compounds only partially dissociate at higher concentrations, the degree of dissociation being concentration dependent.[22] Thermodynamic studies[14-18, 22] have shown that the dissociation tendencies of mercuric (HgX_2) and organomercuric (RHgX) compounds depend upon the nature of X^- as follows:

$$F^- > OCOCH_3^- > HPO_4^{2-} \simeq Cl^- > Br^- > NH_3 > OH^- > SR^- > S^{2-}$$

Thiol and sulfide compounds are particularly stable, i.e., they have very low tendencies to dissociate.

Mercuric[14] and organomercuric[15-18] ions react rapidly with water (hydrolyze) to form corresponding hydroxides (eqs 2, 3, and 5). These reactions are pH-dependent and will not occur to a significant extent in acidic water (pH < 3-4). However, within pH ranges usually found in natural waters (pH 5-9), the ions are almost completely hydrolyzed (Figures 2-4). Experiments discussed later in this report indicate that these hydrolysis equilibria have important effects upon the rates of organomercury reactions in water.

Natural waters contain a variety of chemical species that can undergo "ligand exchange reactions" with mercuric or organomercuric complexes. Ligand exchange reactions involve reaction of mercuric or organomercuric complexes with some chemical species, Y, to form a new complex (eqs 6-8).

$$HgX_2 + Y \rightleftarrows HgXY + X \qquad (6)$$

$$HgXY + Y \rightleftarrows HgY_2 + X \qquad (7)$$

$$RHgX + Y \rightleftarrows RHgY + X \qquad (8)$$

Ligand exchange reactions have been studied by a variety of techniques. Early attempts to measure the rate of reaction of mercuric salts with human serum mercaptalbumin, a protein that contains sulfhydryl groups, were unsuccessful because of the rapid rate of the reaction.[23] Interest in the function of sulfhydryl groups in enzyme catalysis[24] prompted a number of kinetic studies of the reactions of protein-SH groups with organomercuric salts. Pioneering studies by Boyer[25]

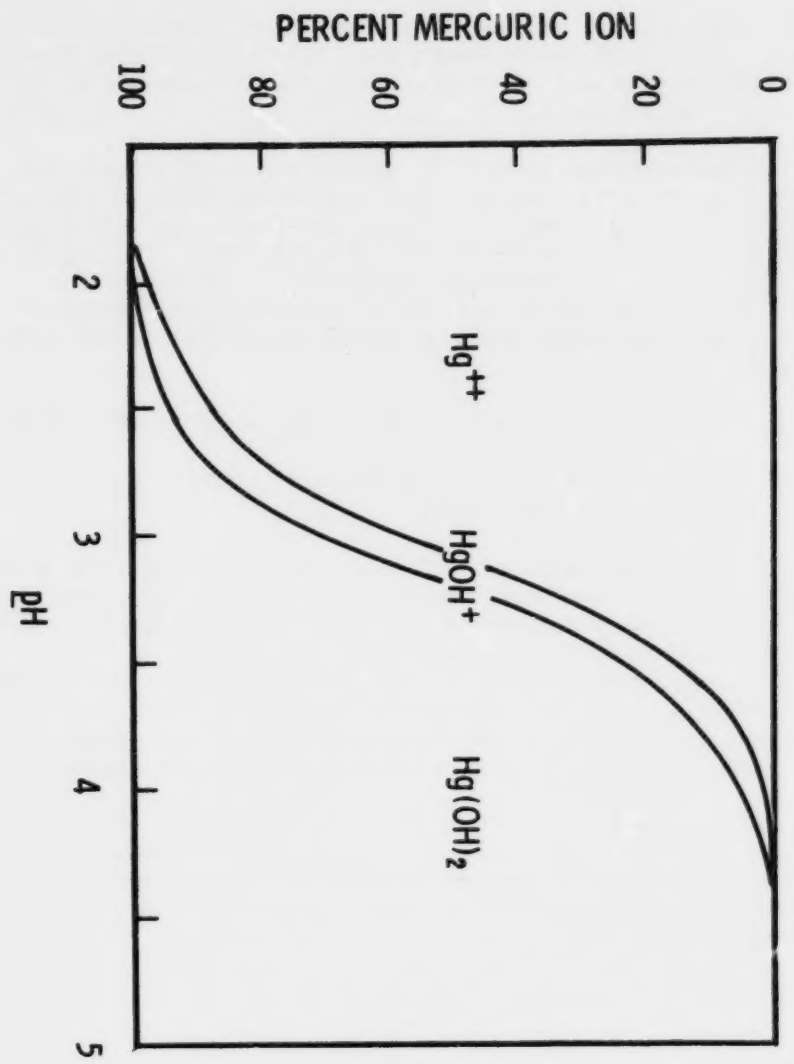


Figure 2. pH dependence of the hydrolysis of mercuric ion.

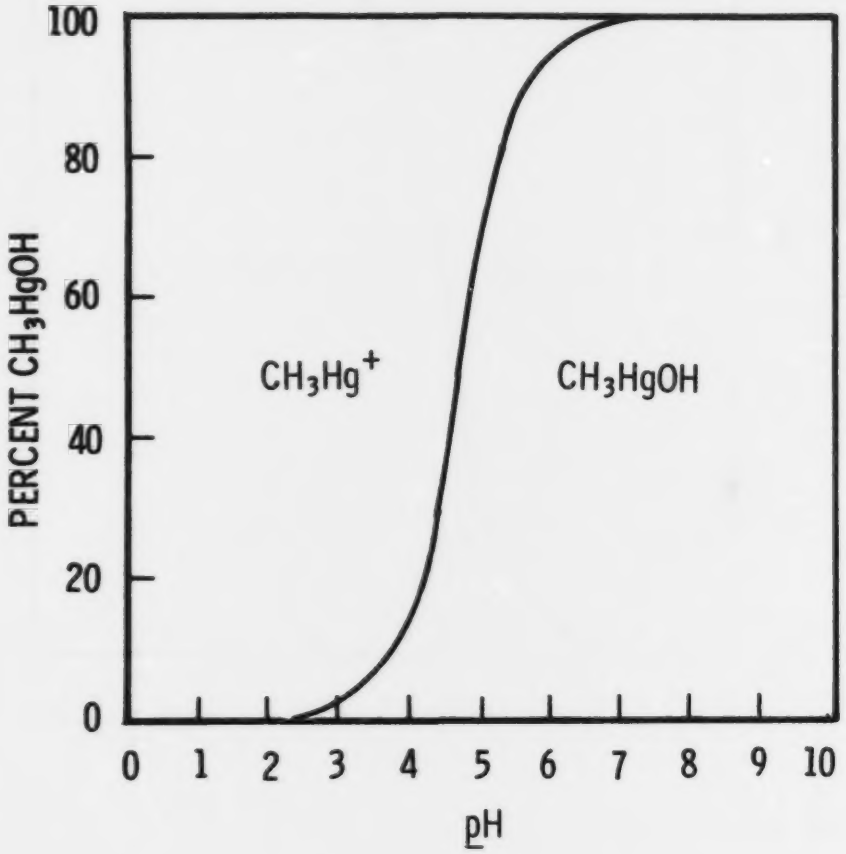


Figure 3. pH dependence of the hydrolysis of methylmercuric ion.

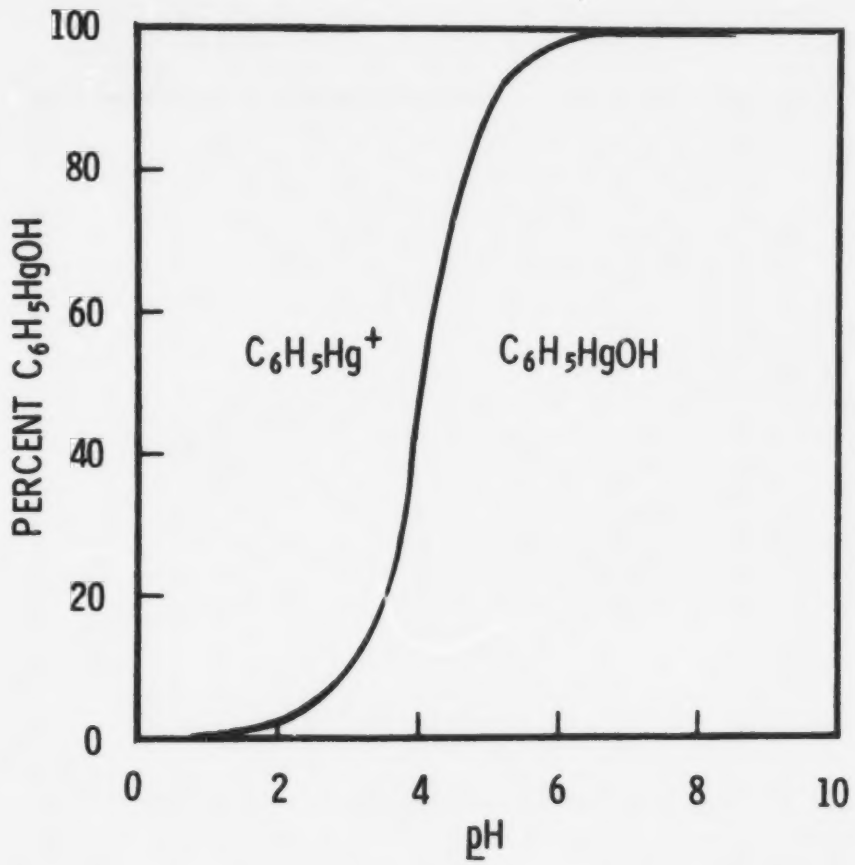


Figure 4. pH dependence of the hydrolysis of phenylmercuric ion.

showed that the reaction of p-chloromercuribenzoate (PMB), a substituted phenylmercury compound, with sulfhydryl groups could be used to distinguish kinetically different types of -SH groups in proteins. Subsequent studies by other groups have established that second-order rate constants for reactions of PMB with protein sulfhydryl groups range from about 10^2 ℓ/mole sec ("masked" -SH groups)[25-28] to 10^5 ℓ/mole sec ("free" -SH groups)[28] at temperatures in the 20-30° C range. Rapid exchange also occurs with complexed divalent inorganic mercury. For example, the sterically hindered reaction of the mercury dimer of serum albumin (ASHgSA) shown below proceeds with a rate constant of 5×10^3 ℓ/mole sec at 24° C.[29]

$$ASHgSA + Hg(HPO_4)_2 \rightarrow 2ASHg(HPO_4) \qquad (9)$$

Presumably, unhindered thiol-mercury complexes would exchange much more rapidly.

Recent work has provided kinetic data on the very rapid exchange reactions involving non-sterically hindered methylmercury complexes. Using the temperature-jump method, Eigen, Geier, and Kruse have determined forward and reverse rate constants for reaction 10.[30]

$$CH_3HgX + OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CH_3HgOH + X^- \qquad (10)$$

Simpson[31] determined rate constants for ligand exchange using the nuclear magnetic resonance technique of Gutowsky and Holm.[32] Rate constants for the exchange reactions frequently were found to be close to diffusion-controlled, with the slowest rate constants about 10 ℓ/mole sec (Table 1). These kinetic data indicate that achievement of ligand exchange equilibrium in systems such as natural waters that contain multiple chemical species and mercury compounds is quite rapid even at the very low concentrations observed in the aquatic environment.

Relative equilibrium concentrations of reduced and oxidized inorganic mercury have been calculated by Hem for a model system containing chloride and sulfate.[33] Hem used these calculations to predict the most stable forms of inorganic mercury in the aquatic environment. No calculations of relative equilibrium concentrations of organomercury complexes under environmental conditions have been reported in the literature. Calculations that we have carried out for methylmercury complexes are discussed later in this report.

CHEMICAL DEGRADATION OF ORGANOMERCURIALS

Kinetic studies of chemical degradation of organomercurials generally have not been carried out in water. Nonetheless, a few relevant studies have been gleaned from the literature.

Table 1. KINETIC DATA FOR ORGANOMERCURY LIGAND EXCHANGE REACTIONS

$$CH_3HgX + Y^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CH_3HgY + X^-$$

X	Y	Log k_f	Log k_r	Reference
Cl^-	OH^-	8.18	4.04	30
Br^-	OH^-	8.08	5.34	30
I^-	OH^-	7.61	6.84	30
SCN^-	OH^-	8.70	5.30	30
SO_3^{2-}	OH^-	6.70	5.40	30
CN^-	OH^-	4.2	8.9	31
CN^-	Cl^-	1.1	9.9	31
CN^-	SO_3^{2-}	2.8	8.8	31
CN^-	$S_2O_3^{2-}$	3.5	6.7	31

Acidolysis reactions of non-ionic organomercury compounds (eq 11) and organomercuric salts (eq 12) have been studied by several investigators.

$$R_2Hg + HX \rightarrow RHgX + RH \qquad (11)$$

$$RHgX + HX \rightarrow HgX_2 + RH \qquad (12)$$

Zimmer and Makower reported that HBr reacted with diphenylmercury ($R = C_6H_5$, eq 11) in 5% water-methanol twice as fast as did HCl.[34] Under these conditions, sulfuric, perchloric, nitric, acetic, and trichloroacetic acids reportedly did not react. In aqueous tetrahydrofuran and dioxane solvents, second-order kinetics were obeyed when HCl was the acid.[35] Reutov and coworkers reported that acidolysis of dibenzylmercury ($R = C_6H_5CH_2$, eq 11) was first-order in dibenzylmercury and first-order overall,[36] but Jensen and Rickborn have strongly criticized Reutov's experimental technique and interpretation.[37] Kinetic data for dimethylmercury acidolysis ($R = CH_3$, eq 11) in water are not available in the literature. Dessy and coworkers reported that the acidolysis of dimethylmercury by HCl in dimethylsulfoxide-dioxane (10:1) was too slow to measure at 40° C.[38] This limited and sometimes confusing information emphasized the need for kinetic studies of acidolysis in water by dissociated acids.

Cleavage of organomercuric salts in water by acids has been investigated. Kreevoy reported the second-order rate constant for acidolysis of methylmercuric iodide ($R = CH_3$, $X = I$), eq 12, by 1 M H_2SO_4.[39] Extrapolation of these data from higher temperatures to 25° C gave the very low rate constant, 3×10^{-9} ℓ/mole sec. Under Kreevoy's conditions the calculated half-life was 3×10^3 days at 25° C. Acidolysis of phenylmercuric chloride ($R = C_6H_5$, $X = Cl$), eq 12, in water containing 10% ethyl alcohol was investigated by Brown.[40] Extrapolating Brown's results to 25° gave a second-order rate constant of 1.7×10^{-6} ℓ/mole sec. Comparison of Kreevoy's and Brown's data indicates that methylmercuric salts undergo acidolysis at much slower rates than phenylmercuric salts.

Another possible route for chemical degradation of organomercuric salts is the so-called "demercuration reaction" shown below.

$$RHgX \xrightarrow{H_2O} ROH + Hg^\circ + X^- \qquad (13)$$

Ouellette[41] has shown that reaction 13 is kinetically first-order and that the reaction rate is very rapid for branched alkylmercuric salts, such as t-butylmercuric and cyclohexylmercuric halides. However, demercuration of methylmercuric salts is very slow. Extrapolation of Ouellette's data for CH_3HgX to 25° gives the first-order

rate constant, 8×10^{-13} sec^{-1} or a half-life of about 3×10^{4} years. No data on demercuration of phenylmercuric salts are available from the literature.

PHOTODECOMPOSITION OF ORGANOMERCURIALS

Most of the abundant literature on the photochemistry of organomercury compounds is concerned with product studies.[10] Upon irradiation, the carbon-mercury bond of organomercurials is cleaved to give alkyl or aryl free radicals and inorganic mercury (eqs 14-17).

$$R_2Hg \xrightarrow{h\nu} R\cdot + \cdot HgR \qquad (14)$$

$$\cdot HgR \rightarrow Hg^{\circ} + R\cdot \qquad (15)$$

$$RHgX \xrightarrow{h\nu} R\cdot + \cdot HgX \qquad (16)$$

$$2\cdot HgX \rightarrow Hg_2X_2 \qquad (17)$$

That alkyl and phenyl free radicals are formed from photolysis of organomercuric salts has been demonstrated by electron spin resonance studies of Janzen and Blackburn.[42]

Quantitative mechanistic studies of organomercury photoreactions are difficult to find in the literature. However, the photolysis of dimethylmercury has been intensely studied. In the vapor phase, dimethylmercury (R = CH_3, eqs 14 and 15) photodecomposed at 30° with a quantum yield of unity to give methyl radicals and elemental mercury.[43] In the liquid phase, a significant fraction of the methyl radicals underwent cage recombination to form ethane, and the remainder abstracted hydrogen atoms to form methane.[44] Although Fagerström and Jernelöv have suggested that photodegradation of dimethylmercury is important in the environment,[45] the insignificant absorption of $(CH_3)_2Hg$ at wavelengths > 280 nm[43] indicates that its sunlight degradation must be very slow. Experiments of Strausz, Do Minh, and Font have shown that photodecomposition of a dialkylmercury compound is extremely slow when wavelengths available from solar radiation, i.e., Pyrex-filtered light (> 290 nm), are employed.[46]

Although no quantum yield data were found for the photodecomposition of phenylmercury compounds or alkylmercuric salts, a few publications on the sunlight stability of these compounds are available. Takehara and coworkers irradiated several phenylmercuric and alkylmercuric compounds with several light sources.[47] Irradiation

of several phenylmercuric salts by an intense 2537Å low-pressure mercury lamp or sunlight resulted in extensive photodecomposition. Photoreaction was more rapid when the compounds were dissolved in water than when they were irradiated as pure solids or in dust formulations. Sunlight irradiation of aqueous phenylmercuric acetate caused 25% decomposition in 10 hours. Major products from photolysis of phenylmercuric acetate and phenylmercuric chloride in water were reported to be Hg_2O and Hg_2Cl_2, respectively. Shiina and coworkers reported results that seemingly conflicted with Takehara's findings. These workers reported that irradiation of phenylmercuric acetate, phenylmercuric chloride, methylmercuric iodide, and several other phenylmercuric salts resulted in little decomposition after light exposure "equivalent to 7 summer days" of sunlight.[48] The apparent conflict in the two publications was probably due to differences in analytical procedures. Takehara analyzed directly for the residual organomercury compounds, whereas Shiina measured the "residual pesticide effect" of the photolyzed organomercurials upon a fungus culture. Comparison of the two publications suggests that the photoproducts also act as effective fungus growth inhibitors.

Taken together, the published studies indicate that sunlight photodecomposition of organomercury compounds may provide an important pathway for conversion of such compounds to inorganic mercury. The lack of quantitative data on the rates of these photoreactions prompted the studies included in this report.

SECTION V

MATERIALS AND METHODS

MATERIALS

Reagent grade dimethylmercury and methylmercuric salts were purchased from various commercial sources. Dimethylmercury was purified by distillation: bp 94-95° (760 mm). Diphenylmercury and phenylmercuric salts were obtained from the Perrine Primate Laboratory, U. S. Environmental Protection Agency, Perrine, Florida. Diphenylmercury was chromatographed on Woelm basic alumina (activity I), and recrystallized from 95% ethyl alcohol. Phenylmercuric acetate was recrystallized from 5% acetic acid in water and phenylmercuric nitrate was recrystallized from 95% ethyl alcohol. Reagent grade mercuric acetate was purified by recrystallization from glacial acetic acid.

Water that was distilled, passed through ion exchange columns, and redistilled was used in all experiments except those carried out with natural waters. The natural water samples were obtained from a pond near Athens, Georgia, and a western North Carolina stream located at the Coweeta Hydrologic Laboratory.

Benzene was acid-washed, dried, and distilled. Other reagent grade solvents were used as received. Cis-1,3-pentadiene was distilled (bp 42-43°, 760 mm), and stored under nitrogen at -20° C. Reagent grade thioglycolic acid and 2-mercaptoethanol were used as received and stored at -20° C. Cysteine hydrochloride and $Na_2S \cdot 9H_2O$ were used without purification. Reagent grade mercuric oxide, acids, and bases were used as received.

ANALYTICAL PROCEDURES

Acidolysis of dimethylmercury was followed by two analytical techniques: (1) gas liquid chromatography (glc) of dimethylmercury on a Porapak QS column using tetrahydrofuran as an internal standard, and (2) a conductometric technique, described in the literature.[38] Aqueous solutions of methylmercuric and phenylmercuric salts were analyzed by the dithizone method of Gran.[49] Phenylmercuric salts were also analyzed by ultraviolet spectroscopy.[50] Diphenylmercury acidolysis in water was followed by ultraviolet spectroscopy, as described by Kaufman and Corwin.[51] Kinetics of the mercuric-salt cleavages of aqueous dimethylmercury and diphenylmercury were determined by measuring the disappearance of mercuric salt by flameless atomic absorption (AA) spectroscopy.[52]

Actual yields for sensitized photolysis of diphenylmercury in benzene were determined by glc on a 3% OV-1 column. Yields for photodecomposition of methylmercury-thiol complexes were measured by nuclear magnetic resonance (nmr) spectroscopy and gas liquid chromatography.[53] Mercury yields in the precipitates resulting from photolysis of phenylmercuric acetate and methylmercury-thiol complexes were measured by digesting the precipitates with aqua regia (3:1 HNO_3-HCl) and determining the mercury by flameless atomic absorption spectroscopy. Yields of benzene from the photolysis of phenylmercury compounds were measured by glc on a Porapak PS column. Product yields in the chemical actinometer were determined by gas liquid chromatography as described elsewhere.[54]

APPARATUS

Kinetic studies of methylmercury and phenylmercury compounds were conducted in a thermostated oil bath that regulated temperature within $\pm$ 0.05° C. One of the major problems in working with DMM was its volatility (vapor pressure 50 mm Hg at 20.5° C),[55a] which made it difficult to accurately weigh and transfer small quantities. In addition, DMM dissolved slowly (several hours) in water. Special bombs were constructed for the studies of dimethylmercury chemical reactions and photolysis (Figure 5). The closed bombs were almost completely filled with solutions to minimize loss of gaseous dimethylmercury. When the stopcock of the bomb was opened, aliquots of the reaction solution were removed by inserting a syringe needle through the septum. The aliquots were analyzed by glc as described above. Control experiments showed that dimethylmercury did not volatilize from the bomb at the elevated temperatures used in the kinetic runs. Dimethylmercury acidolysis was also followed with procedures and apparatus described by Davis and McDonald.[55b,c] Solutions for the conductance studies were prepared and added to the cell under a nitrogen atmosphere in a glove box.

Quantum yield studies were carried out on a photochemical apparatus consisting of a rotating turntable assembly contained in a water bath. A Hanovia 450-W medium pressure mercury lamp, positioned in the center of the turntable, was employed as the light source. The apparatus has been described in detail elsewhere.[56] Samples for photochemical studies were degassed by several freeze-thaw cycles under vacuum.

Glc analyses were performed on a Tracor MT-220 gas chromatograph, equipped with flame detectors and a Ni-63 electron capture detector. Glc peaks were integrated by a Varian Model 477 Digital Integrator. Mass spectra were obtained on a Hitachi-Perkin Elmer RMU-7 Mass Spectrometer. Nmr spectra of the methylmercury-thiol complexes were measured on a Varian HA-100 NMR Spectrometer. Flameless AA analyses were carried out using a Perkin-Elmer 403 Atomic Absorption

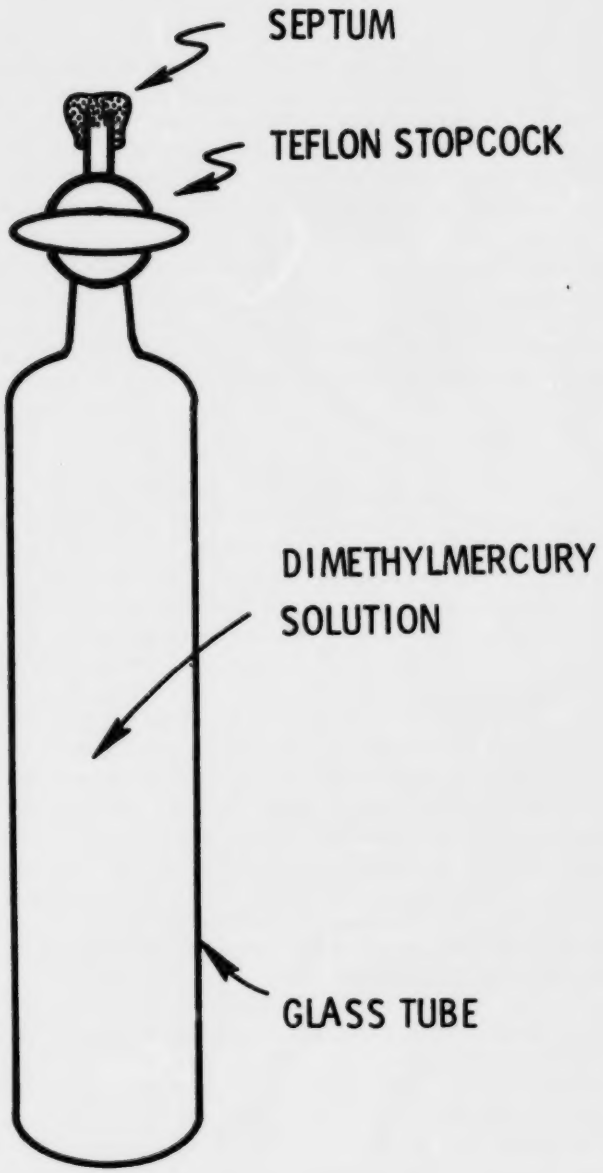


Figure 5. Enclosed bomb for kinetic studies.

Spectrophotometer. Ultraviolet spectra were measured by a Perkin-Elmer 352 Ultraviolet Spectrophotometer and uv analyses were carried out on Bausch and Lomb Spectronic 505 and Beckman DU Spectrophotometers. X-ray diffraction studies were carried out at J. F. Kennedy Space Center, Florida.

ACIDOLYSIS OF DIMETHYLMERCURY, METHOD 1

A weighed portion of dimethylmercury was added to a volumetric flask containing 0.0040 M tetrahydrofuran (the glc internal standard) in water and a magnetic stirring bar. The resulting mixture was stirred for 12 hours to dissolve the dimethylmercury, which was found to have a solubility limit of 0.02 M in water at room temperature. An aliquot of standardized acid solution was added to the aqueous dimethylmercury solution, and the resulting solution was transferred by a syringe to the kinetic bomb (Figure 5), which was then totally immersed in the thermostated oil bath. Periodically, the bomb was removed from the bath and cooled by immersing in water at room temperature. After a 1.0-microliter aliquot was removed from the bomb and analyzed by glc, the bomb was returned to the bath. Second-order rate constants for acidolysis were calculated by computer using a least-square analysis of data.[57]

ACIDOLYSIS OF DIMETHYLMERCURY, METHOD 2

Dimethylmercury was added to water in a volumetric flask containing a magnetic stirring bar. The flask was placed inside the glove box under nitrogen and the dimethylmercury was dissolved by stirring for 12 hours. An aliquot of standardized acid solution was added to the dimethylmercury solution under nitrogen in the glove box, and the resulting solution was transferred to the conductance cell. The cell was immersed in the thermostated oil bath, and the conductance of the solution was recorded at appropriate time intervals. Reactions were carried out with a 100-fold excess of dimethylmercury, and pseudo-first-order kinetics were observed. Pseudo-first-order rate constants were calculated by computer employing a least-squares fit of the data.[57]

MERCURIC SALT CLEAVAGE OF DIMETHYLMERCURY

Aqueous solutions of mercuric perchlorate (10^{-6} to 10^{-9} M) were prepared by the addition of perchloric acid to mercuric acetate solutions. The pH was measured with a pH meter and the initial mercuric salt concentration was measured by flameless AA spectrophotometry. The mercuric perchlorate solution was then transferred to a reaction bomb and the bomb was immersed in the oil bath thermostated at 27.0°. An aliquot of aqueous dimethylmercury solution was added and, at appropriate time intervals, aliquots of the reaction solution were removed and the mercuric salt concentration

was measured by flameless AA spectrophotometry. Control experiments established that the mercuric salt concentration was not decreased by adsorption on the glass walls of the reaction vessel during the time periods of the kinetic runs. Second-order rate constants were calculated as described above.

ACIDOLYSIS OF DIPHENYLMERCURY

Aqueous solutions of diphenylmercury ($\sim 10^{-6}$ M) were prepared by adding weighed amounts of diphenylmercury to water and stirring for several days. Exact concentrations were determined by uv analysis. An aliquot of standardized perchloric acid was added and the rate of disappearance of diphenylmercury was determined by uv spectroscopy.[51]

MERCURIC SALT CLEAVAGE OF DIPHENYLMERCURY

The procedure for the kinetic runs was essentially the same as described above for dimethylmercury with the exception that the mercuric perchlorate and diphenylmercury concentrations were lower (10^{-9} to 10^{-10} M). Attempts to follow the reaction by ultraviolet spectroscopy with 10^{-6} M reactant concentrations were unsuccessful, because complete cleavage occurred within a matter of seconds in neutral and acidic media.

PHOTOCHEMICAL PROCEDURES

Solutions of organomercury compounds were irradiated by broad-band (> 290 nm) and monochromatic (313 nm) light from the mercury lamp. Light from the mercury lamp was filtered through a Pyrex sleeve for the broad-band studies and through a Pyrex sleeve and 1.0 cm of a solution of 0.001 M potassium chromate in 2% aqueous potassium carbonate to isolate the 313 nm line. Procedures for preparing and degassing sample and actinometer tubes have been previously described.[54]

A valerophenone actinometer[58] was used for the studies with 313 nm light and a benzophenone-cis-1,3-pentadiene actinometer[59] was used for the broad-band irradiations. After irradiating the organomercurial and actinometer solutions in parallel in the quantum yield apparatus, quantum yields were calculated by comparing actual yields of photoreaction in the solutions.[54]

Sensitized photolyses were carried out with sufficient concentrations of sensitizers to absorb > 99% of the light. Singlet oxygen was generated by methylene blue sensitization.[60] Quenching studies were carried out under conditions where no light was absorbed by the quenchers. Disappearance quantum yields for phenylmercurials and sulfur-bonded methylmercury complexes were independent of the extent of reaction to at least 35% of completion. All quantum yields were determined at 25° C.

PHOTOLYSIS OF METHYLMERCURIC SULFIDE ION

Aqueous solutions of methylmercuric sulfide ion (0.010 M) were prepared by reacting methylmercuric hydroxide with a two-fold molar excess of sodium sulfide. Photolysis by > 290 nm light caused formation of gas and a black precipitate. The gas was characterized by glc and the precipitate was identified by X-ray diffraction.

Yields of the mercuric sulfide precipitate were determined as follows: (1) The photolyzed solutions were diluted 1:100. Mercuric sulfide is soluble in concentrated sodium sulfide and therefore did not completely precipitate prior to dilution.[61] The diluted solutions were allowed to stand in the dark for 12 hours to ensure complete precipitation. (2) The supernatant liquid was partially decanted and the remaining mixture was centrifuged. (3) After centrifugation, the precipitate was washed with water, recentrifuged, and dissolved in aqua regia. (4) Mercuric ion concentration was determined as usual by atomic absorption spectrophotometry.

SUNLIGHT PHOTOLYSIS OF METHYLMERCURY COMPOUNDS

Aqueous solutions (1.00×10^{-4} M) of methylmercuric hydroxide, methylmercuric chloride, methylmercuric bromide, and methylmercuric iodide were degassed as usual in 10.0 ± 0.1 mm quartz tubes. The tubes were sealed under vacuum and irradiated by September sunlight between 9 AM and 3 PM on the roof of the Southeast Environmental Research Laboratory (SERL), Athens, Georgia. Methylmercuric iodide was irradiated for 3.7 hours and the other methylmercury compounds were irradiated for 17.1 hours.

ACETONE-SENSITIZED PHOTODECOMPOSITION OF PHENYLMERCURIC ION AND PHENYLMERCURIC HYDROXIDE

Degassed aqueous solutions of phenylmercuric perchlorate (1.00×10^{-3} M) and acetone (0.60 M) adjusted to pH 2.3 and pH 10.2 were irradiated by Pyrex-filtered light. Benzene was determined by glc and precipitates were analyzed for mercury content by flameless AA spectrophotometry. Nearly quantitative yields of inorganic mercury precipitated under basic conditions (0.95 mole Hg per mole C_6H_5HgOH decomposed) and lower yields (0.55 mole Hg per mole $C_6H_5Hg^+$ decomposed) precipitated under acidic conditions. Analysis of the supernatant of the acidic solution showed that it contained an additional 0.4 mole Hg per mole $C_6H_5Hg^+$ decomposed, presumably in the form of mercurous and/or mercuric ions.

QUENCHING STUDIES OF PHENYLMERCURY COMPOUNDS

Solutions containing the phenylmercury compound and various concentrations of quencher (0-4 M) were prepared, degassed (unless

molecular oxygen was quencher), and irradiated in parallel at 313 nm on the photochemical apparatus.

SUNLIGHT PHOTOLYSIS OF PHENYLMERCURY COMPOUNDS

Air-saturated solutions of diphenylmercury (1.0×10^{-6} M) and phenylmercuric salts (4.0×10^{-5} M) in water were sealed in 13.0 $\pm$ 0.1 mm quartz tubes. The tubes were irradiated by sunlight in an exposed area on the roof of the Southeast Environmental Research Laboratory, Athens, Georgia. In a preliminary experiment, tubes were irradiated for 18 days during July (average temperature, 30° C during daylight hours). In a second experiment, tubes were irradiated for two days in August (average temperature 31° C). During this period the weather was mostly fair, and the tubes received 20.0 hours of sunlight. Unphotolyzed controls showed no decrease in phenylmercurial concentration during the irradiation periods. Based on the fraction of phenylmercurial that disappeared, photolysis rate constants and half-lives were calculated assuming first-order kinetics.[62, 63]

SECTION VI

RESULTS AND DISCUSSION

CALCULATED EQUILIBRIUM CONCENTRATIONS OF METHYLMERCURIC SPECIES IN AQUATIC SYSTEMS

Although the literature is devoid of quantitative information about formation of organomercury complexes in the environment, previous studies have provided abundant information concerning equilibrium constants for methylmercury complexes in water.[15,18] We have devised a technique utilizing these equilibrium constants to calculate relative concentrations of methylmercury complexes in aqueous systems containing chemical species found in natural waters, i.e., hydroxide, chloride, hydrogen sulfide and its dissociated forms, thiols (RSH), amines (RNH_2), phenols (humic acid), ammonia, and orthophosphate.[64] Bicarbonate and organic carboxylic acids were not considered because they form very weak complexes with the methylmercury moiety. To render these calculations relevant to the aquatic environment, we used recently measured concentrations of chemical species in Lake Erie[65] where high concentrations of mercury have been found in fish.[66]

The Project Hypo study of the Lake Erie central basin hypolimnion showed that high concentrations of hydrogen sulfide are present in the water column near the bottom sediments.[67] Formation of locally high concentrations of hydrogen sulfide is a phenomenon observed in many natural waters.[68] Complexation of the methylmercury group by reduced sulfur species (H_2S, SH^-, and S^{2-}) results in the formation of two species, methylmercuric sulfide ion (CH_3HgS^-) and bis(methylmercury) sulfide ($(CH_3Hg)_2S$).[18] The two species are in equilibrium as shown in equation 18.

$$2CH_3HgS^- + H^+ \rightleftharpoons (CH_3Hg)_2S + SH^- \qquad (18)$$

Our calculations indicate that these two species should account for very high fractions (> 95%) of the methylmercury complexes in natural waters that contain reduced sulfur species (Figures 6 and 7). Relative concentrations of CH_3HgS^- and $(CH_3Hg)_2S$ depend upon the pH and total concentration of reduced sulfur species. At high concentrations of reduced sulfur species (10^{-3} to 10^{-4} M), CH_3HgS^- accounts for virtually all of the complexed methylmercury in the pH 5-9 range (Figure 6). As the reduced sulfur concentration drops, $(CH_3Hg)_2S$ becomes the predominant methylmercury complex in acidic waters (Figure 7) and CH_3HgS^- remains the predominant complex in basic waters (Figure 6).

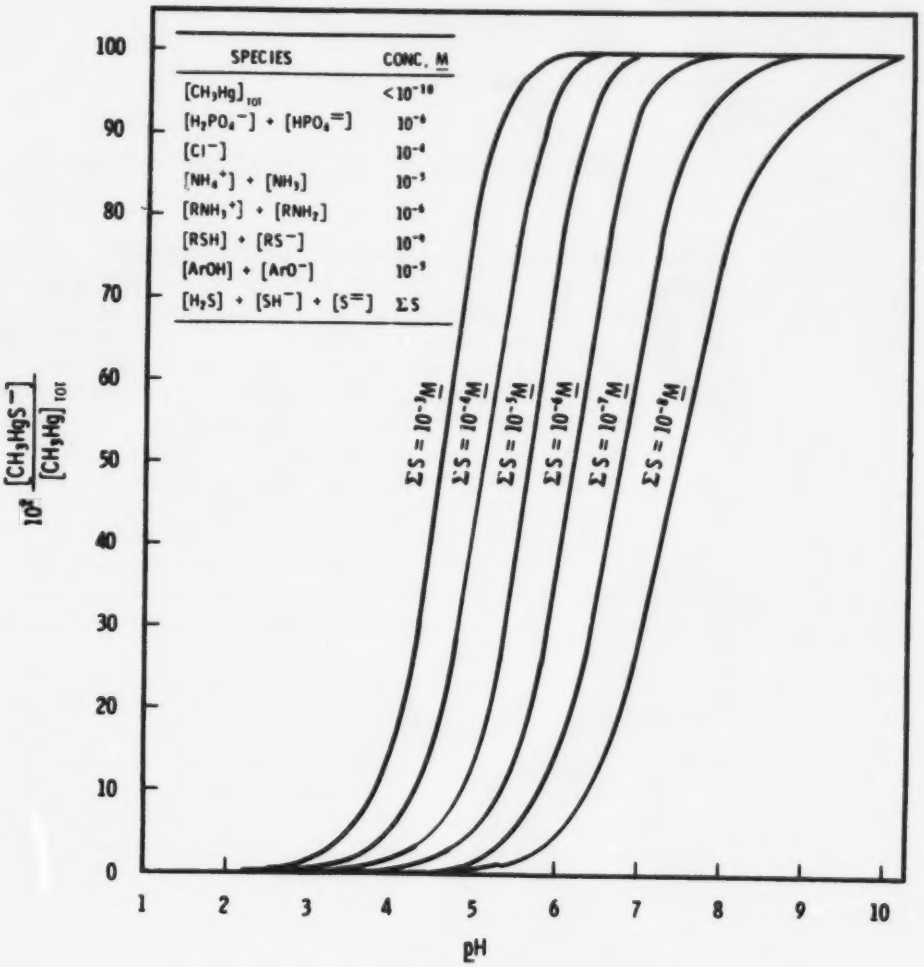


Figure 6. Relative concentrations of CH_3HgS^- in systems containing multiple chemical species.

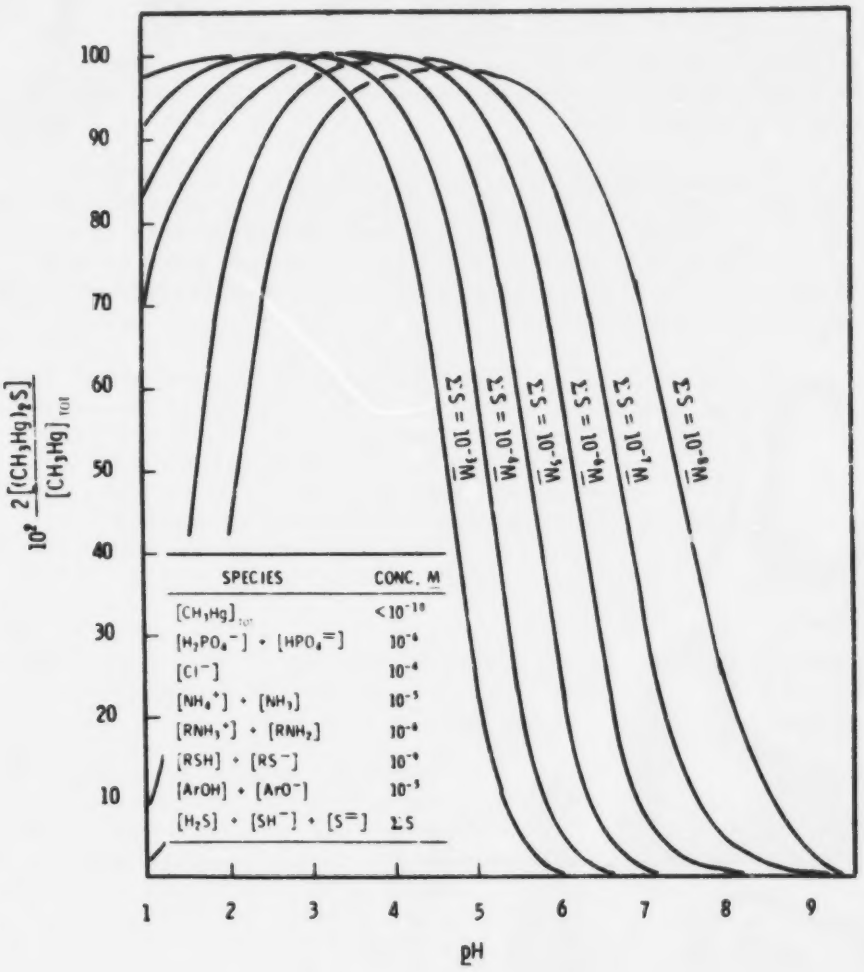


Figure 7. Relative concentrations of $(CH_3Hg)_2S$ in systems containing multiple chemical species.

In solutions containing the chemical species at concentrations indicated in Figure 6, but no reduced sulfur, nearly all the methylmercury would be complexed by organic thiols, e.g., sulfhydryl-containing proteins, in the pH 5-9 range (Figure 8). Thus, when either reduced sulfur species or organic thiols are present in natural waters, methylmercury is quantitatively complexed by sulfur-bonded ligands.

Exclusion of reduced sulfur species and organic thiols from the system permits complexation by more weakly binding chemical species. The plot of calculations shown in Figure 9 indicates that in the absence of sulfides and thiols, methylmercuric hydroxide is the major complex in basic waters (pH 7-10) and methylmercuric chloride predominates in acidic waters.

One noteworthy aspect of the calculations is their prediction that commonly occurring chemical species such as orthophosphate, ammonia, phenolic groups in humic acid, and amino groups in protein have relatively little impact upon complexation of methylmercuric ion under environmental conditions. Moreover, the calculations indicate that methylmercury can be freed from sulfur-bonded complexes by strong acidification. Experiments have also shown that methylmercury can be freed from sediments or biological samples by treating the samples with strong acid.[69]

Equilibrium calculations are strictly applicable only to closed systems, and equilibrium is closely approximated in natural waters only if the rate of approach to equilibrium is more rapid than the rate of change of environmental conditions.[70] Kinetic studies of ligand exchange reactions discussed previously have shown that achievement of equilibrium is very rapid for such reactions. Moreover, the Lake Erie Time Study of Kramer and coworkers indicated that the rate of change in concentration of the chemical species in Lake Erie considered in the above calculations is relatively slow even during periods of high biological activity.[65] Thus, near approach to the calculated equilibrium concentrations of methylmercury complexes is probable in local regions of lakes and slower moving rivers and streams.

Although the literature does not contain a great deal of information concerning equilibrium constants for phenylmercury complex formation,[16,17] sufficient data are available to indicate that relative stabilities of phenylmercury complexes parallel those of methylmercury complexes.

KINETICS OF ORGANOMERCURY REACTIONS IN WATER

Theoretical Considerations

The reaction mechanism, the rate expression, and the rate constant are required to evaluate the significance of a reaction in the

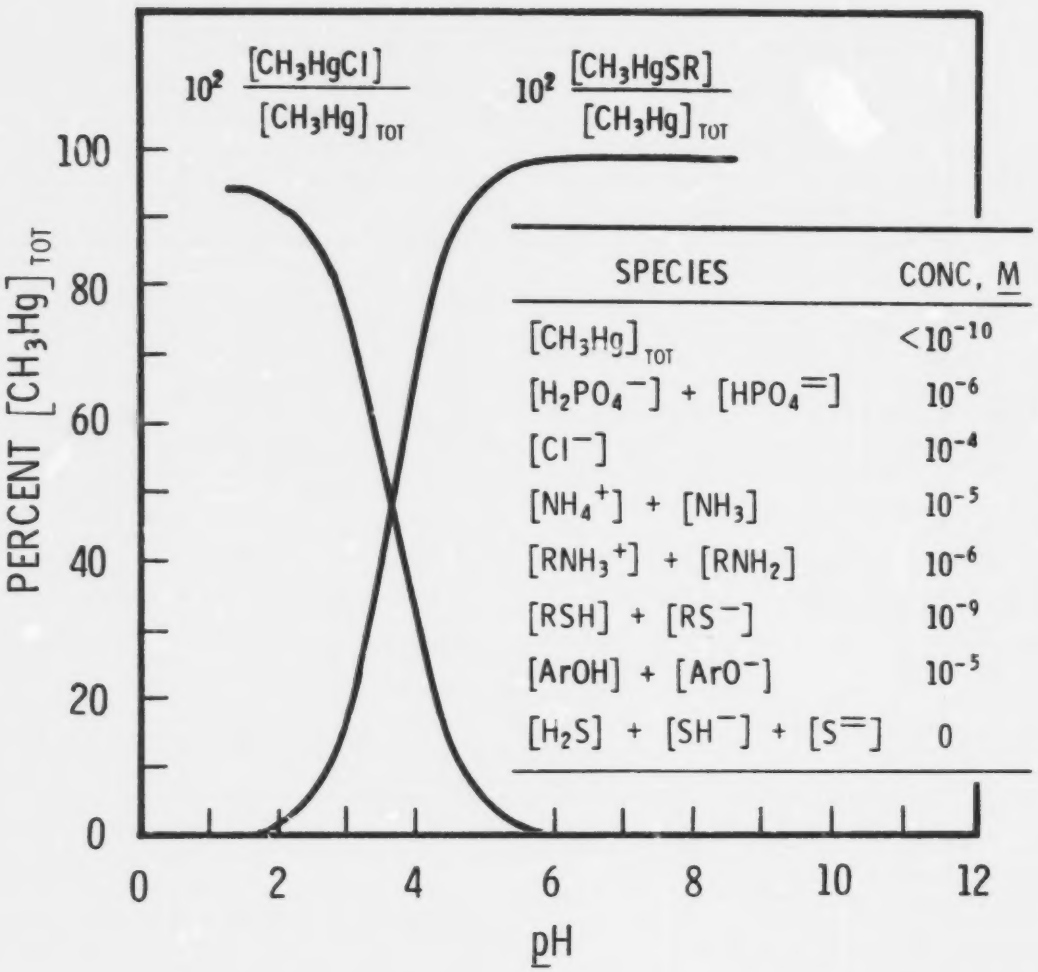


Figure 8. Relative concentrations of CH_3HgCl and CH_3HgSR in systems containing multiple chemical species, excluding reduced sulfur.

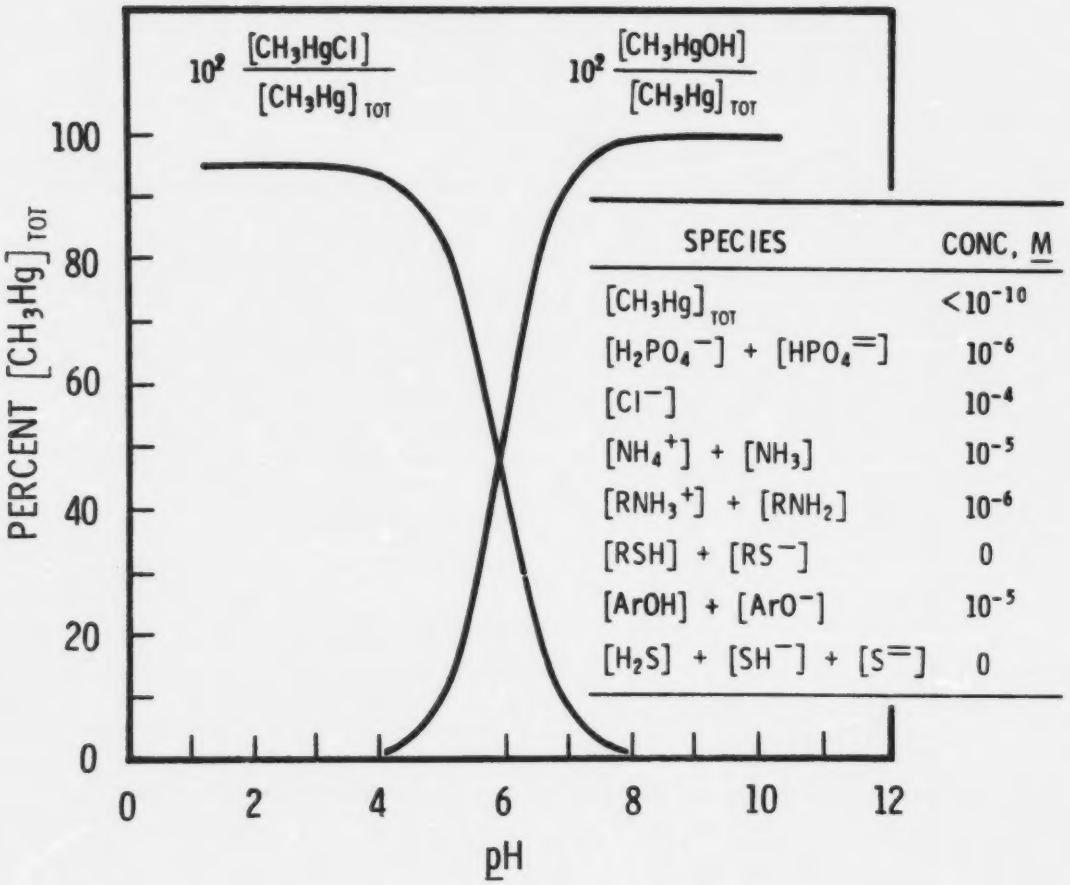


Figure 9. Relative concentrations of methylmercury complexes in systems containing multiple chemical species, excluding reduced sulfur species and organic thiols.

degradation or transformation of a pollutant. Also determination of rate constants at different temperatures will allow calculation of activation parameters, which are indicative of the reaction pathway, and will allow extrapolation of the rate constant to other temperatures. It is desirable to carry out these studies in water when possible because of pronounced solvent effects on rates and products.

Since rate constants are sometimes difficult to relate to the lifetime of a reactant, the half-life ($t_{\frac{1}{2}}$) expression is often employed.[71] The half-life is defined as the time required for the concentration of a reactant to be reduced to one-half its initial concentration.

The $t_{\frac{1}{2}}$ expression is especially convenient for first-order[71] reactions (eq 19). The rate of disappearance of reactant A is given by differential equation 20.

$$A \xrightarrow{k_1} B \tag{19}$$

$$-\frac{d[A]}{dt} = k_1[A] \tag{20}$$

The $t_{\frac{1}{2}}$ expression derived from the integrated form of equation 20 is given in equation 21.

$$t_{\frac{1}{2}} = \frac{0.693}{k_1} \tag{21}$$

The $t_{\frac{1}{2}}$ is independent of the concentration of reactant A and dependent only on the magnitude of the rate constant (k_1).

The $t_{\frac{1}{2}}$ expression for second-order[71] reactions requires a statement of reactant concentrations. The disappearance of reactant A (eq 22), given by equation 23, includes the concentrations of both reactants.

$$A + B \xrightarrow{k_2} C \tag{22}$$

$$-\frac{d[A]}{dt} = k_2[A][B] \tag{23}$$

The derivation of the half-life expression by integration of equation 23 gives an equation too complex to be of practical value. However, in the special case of equal initial concentrations of reactants, the $t_{\frac{1}{2}}$ expression may be expressed as

$$t_{\frac{1}{2}} = \frac{1}{[A]k_2} \qquad (24)$$

where [A] = [B]

Another special case results when the effective concentration of one reactant does not change with time (pseudo-first-order reaction). This occurs when one reactant is present in large excess or its effective concentration does not change with time because of buffering. Half-life of reactant A is dependent only on the concentration of the reactant in excess [B] and the magnitude of the rate constant (k_2) (eq 25).

$$t_{\frac{1}{2}} = \frac{0.693}{[B]k_2} \qquad (25)$$

when $[B] >>> [A]$

A graphical representation of this relationship is given in Figure 10 in which $t_{\frac{1}{2}}$ is plotted as a function of concentration for specific rate constants.

The application of kinetics in terms of the reactivity or transformation of a pollutant requires an understanding of the reaction process and reaction conditions. This is particularly true in extrapolation of laboratory to the aquatic environment.

Acidolysis of Dimethyl- and Diphenylmercury

Cleavage of the carbon-mercury bond by protic acid in dialkyl- or diarylmercury compounds is referred to as acidolysis (eq 26).[6a, b] This reaction has been proposed by several investigators[4, 6a, 72] to be a pathway for the chemical transformation of dimethylmercury to methylmercury derivatives (Figure 1) in the aquatic environment.

$$CH_3HgCH_3 + H^+ + X^- \xrightarrow{H_2O} CH_3Hg^+ + X^- + CH_4 \qquad (26)$$

$$X = Cl^-, Br^-, I^-, ClO_4^-, NO_3^-$$

However, as discussed earlier (Section IV), the rate constant for acidolysis of dialkyl- or diarylmercury compounds in water has not been determined. Even with compounds for which the kinetics have been determined in organic solvents, the reaction mechanisms are not clearly defined.

Preliminary work was done to evaluate a glc method for following the acidolysis kinetics. Although the organomercuric salts were

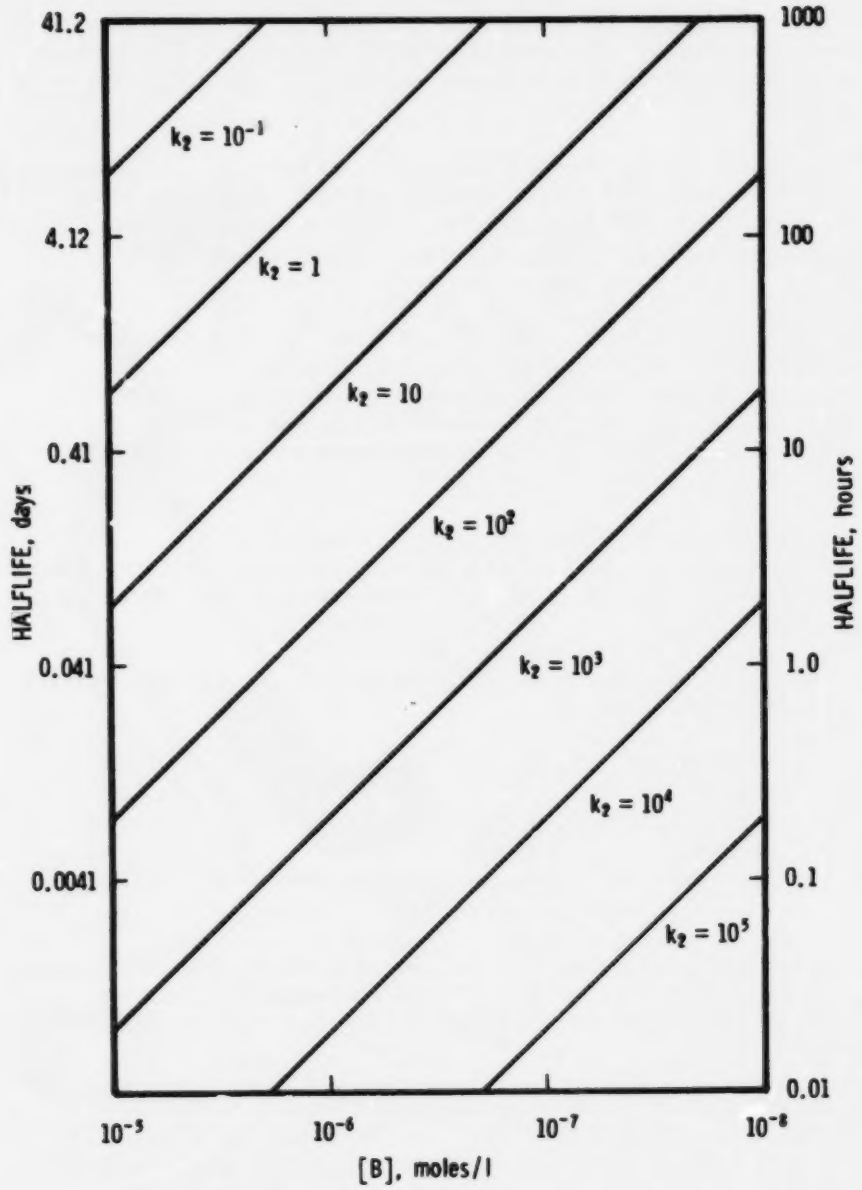


Figure 10. Half-life of A vs. concentration of B for second-order reactions when $[B] >>> [A]$.

found to decompose during chromatography,[73] DMM was found by combined GC-MS to be stable to glc conditions employed. The kinetics of acidolysis were therefore determined by following the disappearance of DMM by this technique. The methyl- and phenylmercuric salts were shown to be stable under the acidolysis reaction conditions, as reported earlier.[40,41]

A plot of the second-order rate expression[71] (Figure 11) indicated that the dimethylmercury acidolysis reactions obeyed second-order kinetics through 50-75% of the reaction. The variation in slope with temperature illustrates the temperature dependence of the reaction.

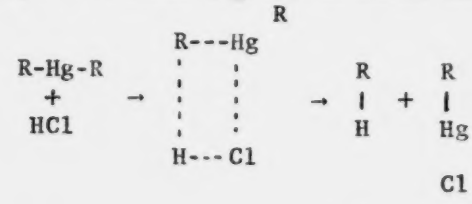
The kinetic data for HCl, HBr, and $HClO_4$ in Table 2 demonstrates that the second-order rate constants are independent of the nature of the acid. In water at the low reactant concentrations indicated, strong mineral acids are completely dissociated and no anion dependence is observed. For HCl the extrapolated rate constant at 25° C is 7.33×10^{-5} ℓ/mole sec.

Verification of the kinetics was obtained by employing a 20-fold excess of HCl compared to DMM and determining the pseudo-first-order rate constant at 40°. The second-order rate constant was obtained by dividing the pseudo-first-order rate constant by the HCl concentration. The constant so obtained, $4.99 \pm 0.13 \times 10^{-4}$ ℓ/mole sec, agrees with the extrapolated value of 5.08×10^{-4} ℓ/mole sec obtained under second-order conditions.

The glc method of determining the reaction velocity was verified by a conductance method[56b,c] employing a large molar excess of DMM compared to HCl. The reaction was followed through 25% to 50% completion by monitoring the decrease of conductance with time. This was possible because of the high specific conductance of H^+ compared to DMM or MMX.[74]

The conductometrically determined rate constants for HCl, $HClO_4$, and HNO_3 are given in Table 3. The calculated second-order rate constants agree with the values reported in Table 2 (glc method) for HCl and $HClO_4$.

The above results definitively show the reaction to be first-order with respect to both DMM and acid (an electrophilic substitution reaction (S_E 2)). Based on stereo-chemical studies, these reactions have previously been thought to proceed by a four-centered or similar type mechanism (S_E i), as shown in equation 27.



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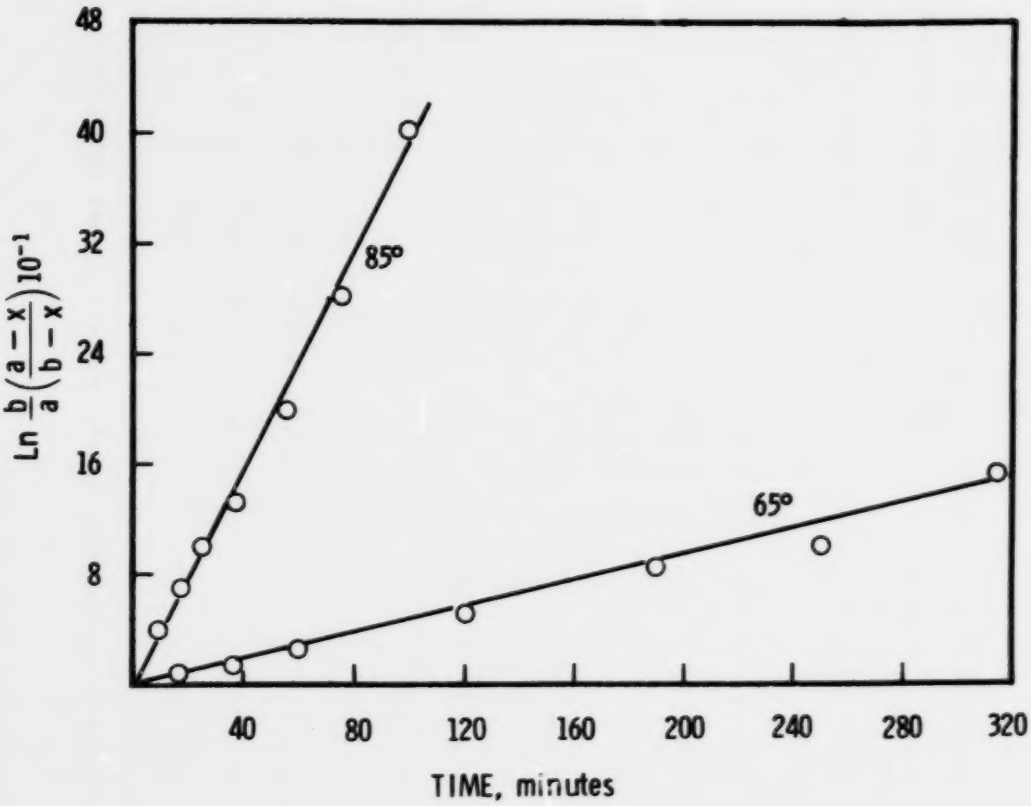


Figure 11. Acidolysis of dimethylmercury.

Table 2. DIMETHYLMERCURY ACIDOLYSIS RATE DATA MEASURED BY GLC[a]

Acid	Conc. Acid M	Conc. DMM M	Temp. °C	k ℓ/mole sec	k sec^{-1}
HCl	8.27×10^{-3}	3.46×10^{-3}	65	$(7.19 \pm 0.32) \times 10^{-3}$[b]	
HCl	8.27×10^{-3}	5.43×10^{-3}	65	$(7.43 \pm 0.19) \times 10^{-3}$[b]	
HCl	8.27×10^{-3}	4.90×10^{-3}	85	$(4.89 \pm 0.07) \times 10^{-2}$[b]	
HCl	8.27×10^{-3}	4.60×10^{-3}	85	$(4.87 \pm 0.39) \times 10^{-2}$[b]	
HCl			40[c]	5.08×10^{-4}	
HCl			25[c]	7.33×10^{-5}	
HCl	1.0×10^{-1}	6.16×10^{-3}	40	5.12×10^{-4}[d]	$(5.12 \pm 0.12) \times 10^{-5}$
HCl	1.9×10^{-1}	5.28×10^{-3}	40	4.87×10^{-4}[d]	$(9.16 \pm 0.09) \times 10^{-5}$
HBr	8.24×10^{-3}	3.47×10^{-3}	85	$(4.46 \pm 0.12) \times 10^{-2}$	
HBr	8.24×10^{-3}	6.82×10^{-3}	85	$(4.69 \pm 0.12) \times 10^{-2}$	
$HClO_4$	8.20×10^{-3}	4.79×10^{-3}	65	$(8.06 \pm 0.33) \times 10^{-3}$	
$HClO_4$	8.20×10^{-3}	6.08×10^{-3}	85	$(5.02 \pm 0.15) \times 10^{-2}$	

[a] See Section V.
[b] The activation parameter based on the average of the two values are $\Delta H^{\ddagger} = 22.1 \pm 0.1$ kcal/mole and $\Delta S^{\ddagger} = -3.1 \pm 0.6$ eu.
[c] Extrapolated.
[d] Calculated from pseudo-first-order rate constant.

Table 3. DIMETHYLMERCURY ACIDOLYSIS RATE DATA DETERMINED CONDUCTOMETRICALLY[a]

Acid	Conc. Acid M x 10^4	Conc. DMM M x 10^2	Temp. °C	Pseudo-First Order Rate Constant k sec^{-1} x 10^4	Second-order Rate Constant[b] k ℓ/mole sec x 10^2
HCl	7.13	1.16	65	0.792	0.70
HCl	7.13	1.07	85	4.12 ± 0.0005	4.0
$HClO_4$	7.20	0.501	65	0.756 ± 0.01	0.78
$HClO_4$	7.20	1.01	85	1.94 ± 0.01	4.1
HNO_3	6.90	1.15	65	0.937 ± 0.48	0.81
HNO_3	6.90	0.52	85	2.70 ± 0.01	5.4

[a] See Section V.
[b] Obtained from pseudo-first-order rate constants.

In the case of protic acid cleavage of DMM in water, where the strong mineral acids are completely dissociated, the reaction probably takes place by a pure S_E2 mechanism (eq 28).

$$\begin{array}{ccccccc} R\text{-}Hg\text{-}R & & R\text{-}Hg^{R} & & R & & R \\ + & \rightarrow & \vdots & \rightarrow & | & + & | \\ H^+ & & H^+ & & H & & Hg^+ \end{array} \qquad (28)$$

Because a myriad of chemical species exist in the aquatic environment, several reactants that might be expected to affect the mechanism were investigated to determine their effect on the rate constant (Table 4). None of the salts tested appreciably affected the rate constant. The small increase noted in some cases may be attributed to a salt effect. Iodide ion, a better nucleophile, complicated the reaction because CH_3HgI precipitated. However, based on the first 20% of the reaction, a rate constant of 7.6×10^{-2} ℓ/mole sec at 85° indicated no apparent rate alteration.

In the presence of $S^=$, the reaction could not be followed because Na_2S addition resulted in interfering glc peaks. However, glc analysis did reveal that DMM was stable to Na_2S (10^{-2} M) at 85° for 24 hours in water.

Since proteins are common to the aquatic environment, an experiment was designed to check for any effect they might have on acidolysis. Cysteine, a thiol-containing amino acid was chosen as a representative compound. The rate constant for the acidolysis of DMM by cysteine hydrochloride is given in Table 4. The kinetics were complicated by the inability to accurately determine the actual H^+ concentration. The acid concentration was obtained by measuring the pH at 65° (pH = 2.32). The rate constants determined were about 50% lower than those obtained with HCl; the possibility of a large rate alteration by proteins was therefore ruled out.

The rate constant for DPM acidolysis by $HClO_4$ was determined in both aqueous ethanol and in water (Table 5). Aqueous ethanol was used because the solubility of DPM in water (10^{-6} M) was too low for convenient determination of the rate constant under second-order conditions. Product studies indicated that the reaction proceeded according to equation 29.

$$C_6H_5HgC_6H_5 + H^+ + ClO_4^- \xrightarrow{H_2O} C_6H_5Hg^+ + ClO_4^- + C_6H_6 \qquad (29)$$

The reaction obeyed second-order kinetics through 50% to 75% completion in both 30% and 40% ethanol-water solutions.

Table 4. DIMETHYLMERCURY ACIDOLYSIS IN THE PRESENCE OF NUCLEOPHILIC SPECIES[a]

Acid	Conc. Acid M	Conc. DMM M	Temp. °C	k ℓ/mole sec	Nucleophile
HCl	8.27×10^{-3}	3.40×10^{-3}	85	$(5.13 \pm 0.05) \times 10^{-2}$	1.03×10^{-2} M NaCl
HCl	8.27×10^{-3}	5.72×10^{-3}	85	$(4.90 \pm 0.07) \times 10^{-2}$	
Cysteine-HCl[b]	7.11×10^{-3}	6.36×10^{-3}	65	$(4.54 \pm 0.14) \times 10^{-3}$	--
Cysteine-HCl[b]	7.84×10^{-3}	5.60×10^{-3}	85	$(3.48 \pm 0.08) \times 10^{-2}$	--
HCl	8.27×10^{-3}	3.50×10^{-3}	85	$(7.61 \pm 0.02) \times 10^{-2}$	1.02×10^{-2} M NaI
HCl	1.0×10^{-2}	5.05×10^{-3}	85		Na_2S

[a] Gas-liquid chromatography technique (see Section V).
[b] pH 2.23.

Table 5. DIPHENYLMERCURY ACIDOLYSIS RATE DATA

Temp. °C	% Ethanol in Water	Conc. DPM M	Conc. $HClO_4$ M	k sec^{-1} x 10^4	k ℓ/mole sec x 10^1	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ eu
70	40	8.80×10^{-5}	2.40×10^{-4}		1.88 ± 0.07		
70	40	8.80×10^{-5}	2.40×10^{-4}		1.69 ± 0.07		
70	30	8.80×10^{-5}	2.40×10^{-4}		1.44 ± 0.04		
70	30	8.80×10^{-5}	2.40×10^{-4}		1.31 ± 0.05		
70	0	1.02×10^{-5}	1.37×10^{-3}	(7.80 ± 0.3)	5.69 ± 0.19	18.1	-7.0
50	0	1.02×10^{-5}	1.37×10^{-3}	(1.53 ± 0.02)	1.12 ± 0.02		
25					9.67×10^{-3}[a]		

[a] Extrapolated value.

When the pseudo-first-order rate constant was determined in water using a large excess of $HClO_4$, the reaction obeyed first-order kinetics through one half-life (see Figure 12).[71]

The rate constant increased as the ethanol concentration was reduced from 30% to 0%. Although the rate increase was small for such a large solvent change, qualitatively it agrees with that expected from the increase in acidity with decreased ethanol concentration.[75] The small decrease in rate constant in going from 40% to 30% ethanol was probably due to solvation effects that could not be evaluated without further study.

Extrapolation of the rate data obtained at higher temperatures to 25° gives a constant of 9.67×10^{-3} ℓ/mole sec for water.

The acidolysis half-lives for DMM and DPM can be calculated at 25° from these data (Tables 2 and 5). Assuming that the acid concentration remains constant because of buffering, pseudo-first-order conditions would prevail (see eq 25 where $[B] = [H^+]$). At pH's commonly found in the environment, DMM would have a relatively long half-life. For example, at pH 5, $t_{\frac{1}{2}}$ would be 33 years at 25°. For DPM under the same reaction conditions, it would be 0.25 years. Thus, acidolysis may be important for DPM under certain conditions, but for DMM it would be important only at low pH's.

The literature contains limited quantitative data on the relative rates of acidolysis for dialkyl- and diarylmercurials. However, a qualitative order of reactivity is given by Kharasch and Grafflin[76] (Table 6). They did not measure actual rates, but rather determined relative rates using unsymmetrical organomercurials in competition studies. They also demonstrated that the relative order of reactivity did not change for a variety of acids and solvent systems. Our data for DMM and DPM are in agreement with this order.

Since the phenyl group is the most reactive moiety listed in Table 6 and acidolysis of DPM is low under environmental conditions, other organomercurials containing the alkyl groups listed would react even slower.

Desymmetrization of Dimethyl- and Diphenylmercury

Carbon-mercury bond cleavage of dialkyl- or diarylmercury compounds by mercuric salts is termed desymmetrization[6a, b] (eq 30). The equilibrium for this reaction generally lies far to the right as shown in Table 7.

$$R_2Hg + HgX_2 \underset{\text{symmetrization}}{\overset{\text{desymmetrization}}{\rightleftharpoons}} 2RHgX \qquad (30)$$

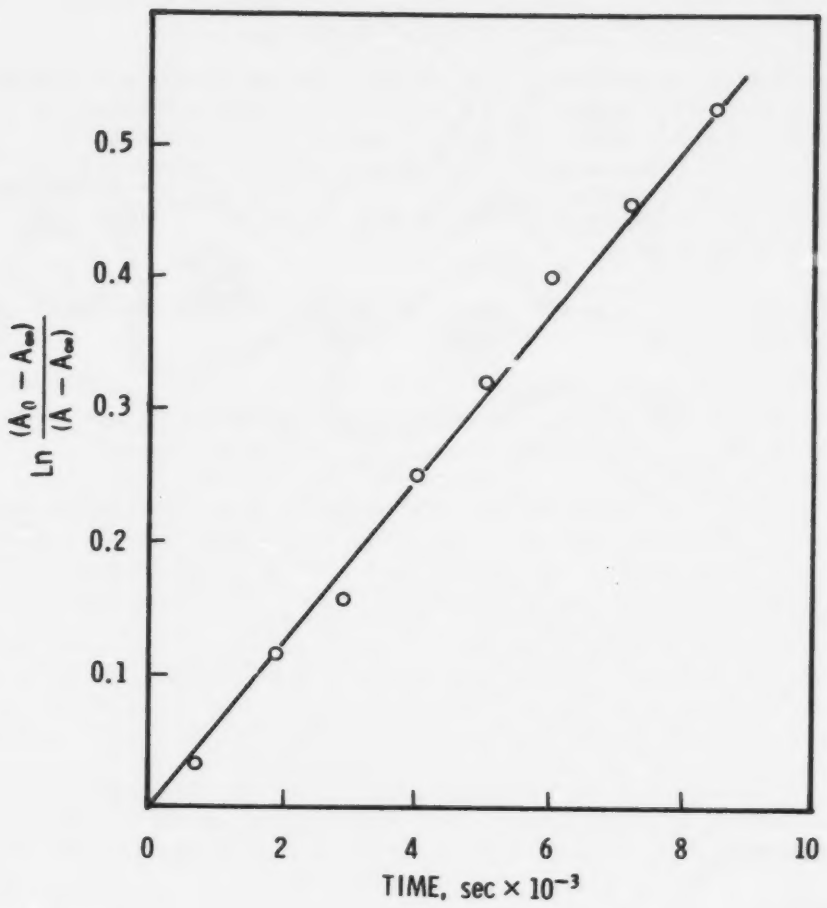


Figure 12. Acidolysis of diphenylmercury.

Table 6. INCREASING EASE OF ACID CLEAVAGE OF ARYL AND ALKYL GROUPS IN ORGANOMERCURIALS[76]

1. Methyl	5. Benzyl
2. Ethyl	6. Cyclohexyl
3. η-Butyl	7. Phenyl
4. η-Propyl	

Table 7. CALCULATED EQUILIBRIUM CONSTANTS FOR THE REACTION OF DIMETHYLMERCURY WITH MERCURIC HALIDES (EQ 30, R = CH_3)[77a]

Salt	K
$HgCl_2$	3.5×10^{11}
$HgBr_2$	2.5×10^{9}
HgI_2	3.4×10^{5}

Kinetic data for the desymmetrizations of DMM and DPM by $Hg(ClO_4)_2$ are summarized in Tables 8 and 9, respectively. Rate constants were obtained by use of the integrated second-order rate expression,[71] which was obeyed through two half-lives as shown in Figure 13.

In the kinetic studies, $Hg(ClO_4)_2$ formed by the reaction of $Hg(OAc)_2$ with perchloric acid gave results identical to those obtained with $Hg(ClO_4)_2$ formed by reacting HgO with $HClO_4$. The perchlorate was chosen because it is completely dissociated in aqueous solution, eliminating interference by any associated salt, which simplifies the reaction kinetics (see Section IV).

The desymmetrization rate constants for DMM and DPM show a strong pH dependence varying six orders of magnitude over the pH range of 1 to 9. The reaction velocity for DPM at pH 2 was so fast (near diffusion controlled) that the rate constant could only be estimated by single-point determinations. The rate constant obtained (2×10^8 ℓ/mole sec) therefore represents a lower limit. A calculation of acidolysis half-lives at the pH's employed indicates that acidolysis was not a competing reaction under the conditions of the desymmetrization reactions.

The strong pH dependency of the desymmetrization reaction may be due to the dependence of the concentration of the various mercuric species on pH. The hydrolysis of mercuric ion (eqs 31 and 32) involves three different mercuric species (Hg^{++}, $HgOH^+$, and $Hg(OH)_2$) whose relative concentrations are a function of hydronium ion concentration.

$$Hg^{++} + H_2O \rightleftharpoons Hg^+OH + H^+ \qquad (31)$$

$$Hg^+OH + H_2O \rightleftharpoons Hg(OH)_2 + H^+ \qquad (32)$$

Figure 2 (Section IV) presents a plot of relative mercuric ion concentration as a function of pH. Below pH 1.5 the predominant mercuric species is Hg^{++} and above pH 4.5 the predominant species is $Hg(OH)_2$. Between pH 1.5 and 4.5, the third species, Hg^+OH, never exceeds about 10% of the total mercuric species.

At low pH's desymmetrization is primarily due to electrophilic attack by Hg^{++} on the organomercurial, represented in equation 33 as a pure S_E2 mechanism. The reaction at pH 9 is attributed to electrophilic attack by $Hg(OH)_2$, represented in equation 34 as an S_Ei mechanism. A pure S_E2 mechanism is probably also operative for Hg^+OH.[6a]

Table 8. pH DEPENDENCE FOR DESYMMETRIZATION OF DIMETHYLMERCURY AT 27°[a]

pH[b]	$Hg(ClO_4)_2$ M	DMM M	k ℓ/mole sec
1.2	7×10^{-8}	7×10^{-8}	5×10^{4}
3.1	7×10^{-8}	5×10^{-8}	2×10^{4}[c]
5.8	3×10^{-7}	3×10^{-7}	1×10^{3}[c]
9.0	2×10^{-5}	1×10^{-5}	2×10^{-1}[c]

[a] Using atomic absorption.
[b] pH determined at start and end of reaction.
[c] Calculated by computer program.

Table 9. pH DEPENDENCE FOR DESYMMETRIZATION OF DIPHENYLMERCURY BY MERCURIC PERCHLORATE AT 27°[a]

pH[b]	Conc. $Hg(ClO_4)_2$ M	Conc. DPM M	k ℓ/mole sec
2.0	2.0×10^{-10}	1.0×10^{-10}	$> 2 \times 10^{8}$[c]
4.8	5.0×10^{-9}	4.1×10^{-9}	3×10^{8}[d]
5.8	7.0×10^{-9}	4.5×10^{-9}	3×10^{5}[e]
6.9	5.2×10^{-8}	4.6×10^{-8}	4×10^{4}[e]
8.1	6.57×10^{-8}	4.56×10^{-8}	3×10^{3}[e]
9.4	1.06×10^{-7}	2.6×10^{-6}	3×10^{3}[e]

[a] Using atomic absorption.
[b] pH determined at the start and end of the reaction.
[c] Lower limit.
[d] Calculated from three single point determinations.
[e] Calculated by computer program.

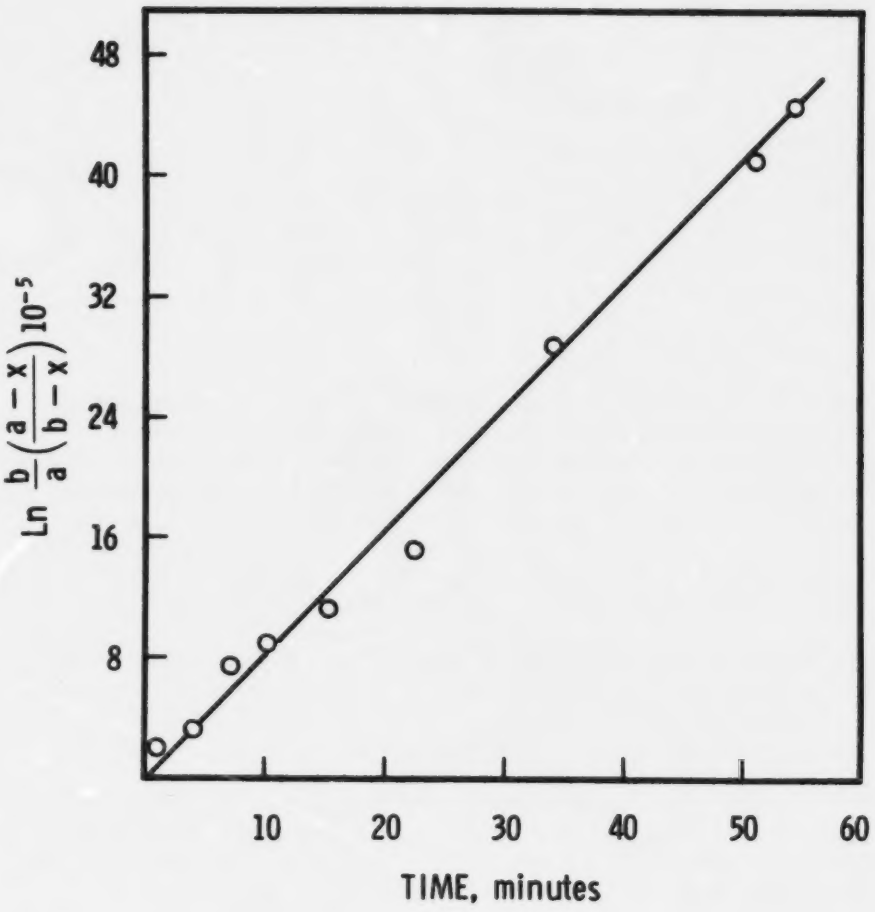
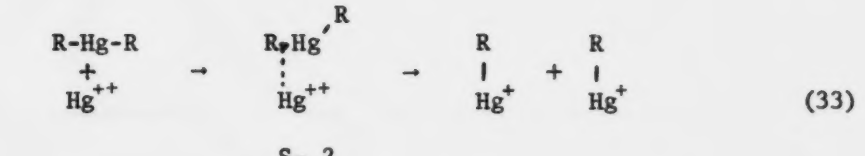
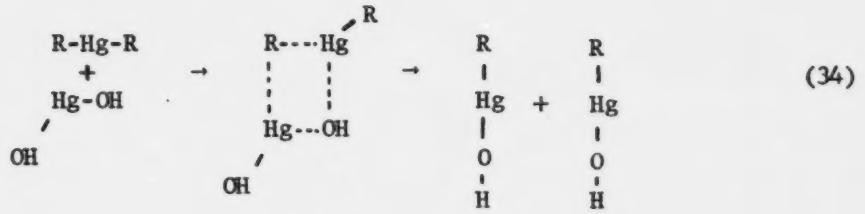


Figure 13. Desymmetrization of dimethylmercury by mercuric perchlorate.



(33)

$S_E 2$



(34)

$S_E i$

The high rate of electrophilic substitution by Hg^{++} as compared to $Hg(OH)_2$ represents about five orders of magnitude in increased electrophilicity towards the carbon-mercury bond. Although extensive background data are not available to evaluate the desymmetrization reaction for other mercuric species, the more electropositive the mercury atom, the larger the rate constant. For example, in ethanol the order of reactivity is $Hg(NO_3)_2 > Hg(OAc)_2 > Hg(Br)_2$, which is also the order of decreasing ionic character of the mercury bond.[77b]

The reverse reaction, symmetrization (eq 30) has been suggested as a possible chemical pathway for the conversion of methylmercuric ion to DMM.[45] It was proposed that the equilibrium would be shifted to the left by removal of mercuric ion as insoluble mercuric sulfide.

A maximum value for the symmetrization rate constant can be obtained from equilibrium data ($K_{eq} = k_{desym}/k_{sym}$). Experiments showed that the equilibrium constant (K_{eq}) was $> 10^4$; thus the rate constant for symmetrization must be four orders of magnitude smaller than that for desymmetrization. Using a methylmercuric hydroxide concentration of 1 ppb (4×10^{-9} M) and the second-order rate constants in Table 8, calculations (eq 24) show this reaction to have a half-life of several years.

The effect of sulfide on the symmetrization reaction was examined employing 0.4 M sodium sulfide and 0.1 M methylmercuric hydroxide in water at 25°. At the end of 24 hours, the organomercurial was 25% reacted. The second-order rate constant derived from these data was $\sim 10^{-6}$ ℓ/mole sec, too low to permit the reaction to be environmentally significant.

Based on the rate constants (Tables 8 and 9), half-lives can be calculated, under pseudo-first-order reaction conditions, where

$[Hg^{II}]$ ($[Hg^{II}] = [Hg^{++}] + [HgOH^{+}] + [Hg(OH)_2]$) is in excess. Using a value of 0.03 ppb for $[Hg^{II}]$ and $k = 1 \times 10^3$, at pH 5.8 (25°), the half-life for reaction with DMM is about 50 days. For DPM under the same conditions, the half-life would be four hours.

Dimethylmercury Stability to Oxygen and Base

DMM was shown to be stable to 1 M KOH. After heating for 24 hours at 85°, glc analysis showed that DMM had not reacted. Likewise DMM neither reacted with KI (five hours at 85°) nor did it react with a saturated solution of egg albumin (2½ hours at 30°).

Secondary and tertiary dialkylmercury compounds are reported to undergo slow oxidation by oxygen in organic solvents.[66] Primary dialkylmercury compounds are less susceptible to oxidation. DMM reaction could not be detected by glc analysis after standing for 20 hours at 85° in an aqueous solution saturated with oxygen. Lack of reaction under these stringent conditions precludes any significant contribution to degradation in the environment.

Evaporative Loss

Evaporative loss of organomercurials from the aquatic environment is a physical process, but because of its potential importance as a means of transport, it is discussed here. Many organomercurials have a substantial vapor pressure. Although the ionic or polar covalent mercurial salts when dissolved in water will not be readily lost to the atmosphere because of solvation effects, mercury and dimethylmercury are non-ionic compounds and evaporative loss may be important.

An estimate of the magnitude of loss may be obtained by employing the method and data of Tsivoglou.[78] Using the relationship between transfer coefficients and molecular diameters ($K_1/K_2 = d_2/d_1$) and van der Waals radii[61] to calculate molecular diameters, the ratio of transfer constants for DMM to oxygen is calculated to be 2.4. Utilization of Tsivoglou's[78] experimental data reveals that for a moderately turbulent river section, DMM would have an evaporative half-life of about 12 hours. This relationship also predicts that dissolved elemental mercury would be lost from the river at a rate 2.3 times faster than DMM.

KINETICS OF ORGANOMERCURY PHOTODECOMPOSITION

Since tropospheric solar radiation has negligible intensity at wavelengths less than about 290 nm (Figure 14),[62,79] systems must have appreciable absorptivity at wavelengths greater than 290 nm if significant photoreaction is to occur in sunlight. Predictions of sunlight photoreactivity can be derived from laboratory experiments employing Pyrex-glass filtration of light from a mercury lamp since this filter transmits only wavelengths greater than 290 nm.[80]

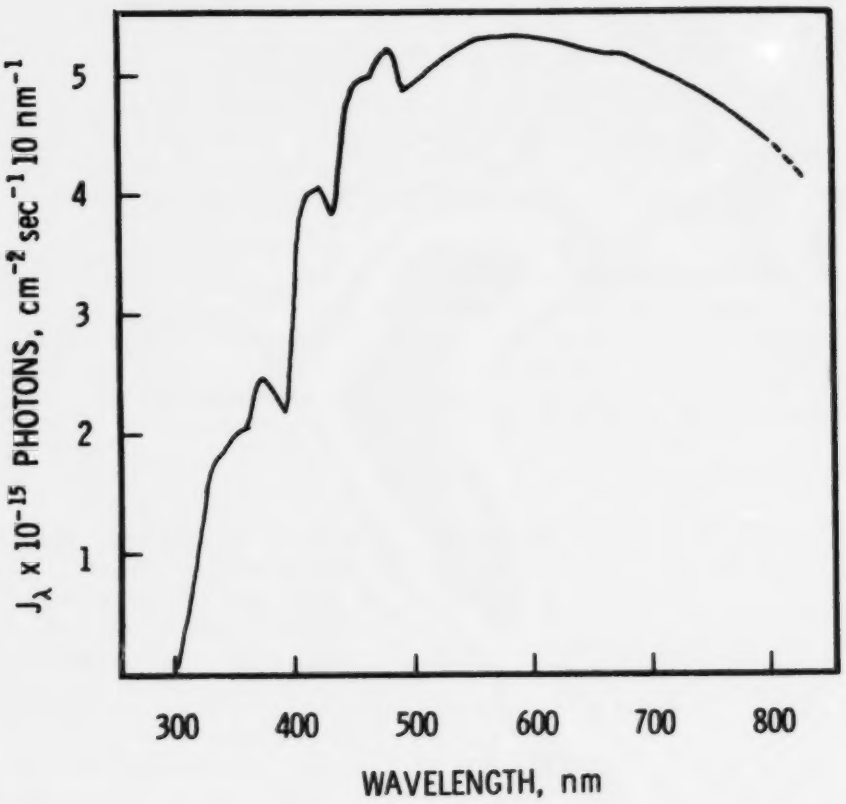


Figure 14. Estimated solar irradiance at solar zenith angle = 0^{o}.[62]

Quantitative calculations of sunlight photolysis rates can be made from specific absorption rates (k_a) and quantum yields (ϕ) both determined in the laboratory.[81] Concentrations of pollutants such as organomercury compounds are generally so low that absorption at wavelengths greater than 290 nm is very weak. For weakly absorbing systems, rates of sunlight photodecomposition (-d[RHgX]/dt) can be expressed as

$$-\frac{d[RHgX]}{dt} = k_a \phi [RHgX] \tag{35}$$

where the term [RHgX] represents concentration of organomercury compound. This equation assumes that sunlight photodecompositions follow first-order kinetics.

Specific absorption rates for the organomercurials were calculated using solar radiation data published by Leighton[62] and extinction coefficients at wavelengths > 290 nm. Leighton's data are most appropriate for Los Angeles during August through November, the period we used for our experiments in sunlight. Since Athens, Georgia, has about the same latitude and elevation as Los Angeles, the spectral flux distribution of sunlight at Athens should closely parallel that at Los Angeles. The value of k_a changes during the day because the solar spectrum is a function of the solar zenith angle, z. For this reason, it is convenient to use an integrated specific absorption rate constant, $(k_a)_{int\,g}$ for predictions of sunlight photolysis rates.[82]

$$(k_a)_{int\,g} = \int_{z=-\pi/2}^{z=\pi/2} k_{az}\, dz/\pi \tag{36}$$

In the above expression, k_{az} is the absorption rate constant at solar zenith angle, z. The half-life ($t_{\frac{1}{2}}$) for a photoreaction can then be expressed as

$$t_{\frac{1}{2}} = \frac{0.693}{(k_a)_{int\,g}\phi} \tag{37}$$

Specific absorption rate constants in natural waters are also a function of competitive light absorption by water and other sunlight-absorbing species, light scattering, and other factors.[83] In this study, the primary purpose was to determine <u>minimum</u> half-lives for photodegradation of organomercury compounds by sunlight, <u>i.e.</u>, half-lives for sunlight photolysis near the surface of a body of water. Using the results of this study, it is possible to predict

photolysis rates of organomercurials at various depths in natural waters by measurements of sunlight intensities.

Light absorption by an organomercury compound may be expressed by the equation

$$(RHgX)^{\circ} \xrightarrow{h\nu} (RHgX)^{*} \qquad (38)$$

where $(RHgX)^{\circ}$ and $(RHgX)^{*}$ represent the compound in its ground and electronically excited states, respectively. The primary quantum yield for any photochemical process is simply the fraction of electronically excited molecules that undergo the process. If the electronically excited molecule undergoes two or more competitive primary photoprocesses, the sum of the quantum yields for these processes is unity, but the quantum yield for a specific process is less than unity. In liquid-phase photochemistry, the measured quantum yield for photoreaction of a compound is often affected by secondary chemical reactions. For example, the primary quantum yield for photocleavage of an organomercury compound (eq 39) may be high, but the measured quantum yield may be lower because of the secondary reaction in equation 40.

$$(RHgX)^{*} \rightarrow R\cdot + \cdot HgX \qquad (39)$$

$$R\cdot + \cdot HgX \rightarrow (RHgX)^{\circ} \qquad (40)$$

Photodecomposition of weakly absorbing compounds can often be accelerated by addition of other compounds that absorb light more strongly. Such acceleration, or photosensitization, can result from electronic energy transfer from the strong light-absorber or sensitizer (S) to the photoreactive compound (eq 42).[84, 85]

$$(S)^{\circ} \xrightarrow{h\nu} (S)^{*} \qquad (41)$$

$$(S)^{*} + (RHgX)^{\circ} \rightarrow (S)^{\circ} + (RHgX)^{*} \qquad (42)$$

Since numerous substances that absorb sunlight more strongly than organomercury compounds are present in natural waters, one goal of this study was to define those types of compounds that can photosensitize degradation of organomercurials.

Quantum yields for photoreactions are sometimes lowered by energy transfer from the electronically excited, photoreactive molecule to a quencher molecule (Q).[85]

$$(RHgX)^{*} + (Q)^{\circ} \rightarrow (RHgX)^{\circ} + (Q)^{*} \qquad (43)$$

The effect of added quencher upon the quantum yield is defined by the following Stern-Volmer expression,

$$\frac{\phi_o}{\phi_Q} = 1 + k_q \tau [Q] \qquad (44)$$

where ϕ_o and ϕ_Q are quantum yields without and with added quencher, respectively, k_q is the bimolecular rate constant for the quenching process, and τ is the lifetime of the excited, photoreactive molecule in the absence of added quencher. Since several excellent quenchers, such as oxygen, are present in the aquatic environment, the effect of known quenchers upon photodecomposition rates of organomercury compounds was also examined.

Photodecomposition of Dimethylmercury, Methylmercuric Ion, Methylmercuric Hydroxide, and Methylmercuric Halides

The ultraviolet absorption spectra of $(CH_3)_2Hg$, CH_3Hg^+, and CH_3HgOH in water revealed that these species absorb virtually no light at wavelengths greater than 290 nm (Figure 15). Specific absorption rate constants for these species are extremely low, so sunlight photolysis rates are very slow. Spectral predictions of low sunlight photoreactivity were corroborated by irradiating aqueous solutions of $(CH_3)_2Hg$, CH_3Hg^+, and CH_3HgOH with Pyrex-filtered ultraviolet light from a mercury lamp. Prolonged irradiations resulted in no photodecomposition of these species.

Other laboratory experiments showed that the decomposition of these methylmercury species was not photosensitized by acetone, a high energy sensitizer (triplet energy, 80 kcal $mole^{-1}$). Moreover, dimethylmercury was not degraded by singlet oxygen, a chemical species important in environmental chemistry.[86]

Sunlight irradiation of aqueous 10^{-4} M solutions of methylmercuric hydroxide, methylmercuric chloride, methylmercuric bromide, and methylmercuric iodide resulted in rapid photodecomposition of CH_3HgI, slow photodecomposition of CH_3HgBr, and negligible degradation of CH_3HgCl and CH_3HgOH (Table 10). Dark controls at the same temperature (30°) showed no change. These and following results demonstrate that changes in the ligand bonded to methylmercury markedly affect photoreactivity.

Facile photodecomposition of CH_3HgI could cause significant errors in the analysis for methylmercury content of environmental samples since several widely used procedures call for gas chromatographic analysis of methylmercuric iodide in organic solvents.[53, 73, 87] Because methylmercuric iodide is photodecomposed by fluorescent lights, precautions should be taken to shield the CH_3HgI solutions from light during the analysis.

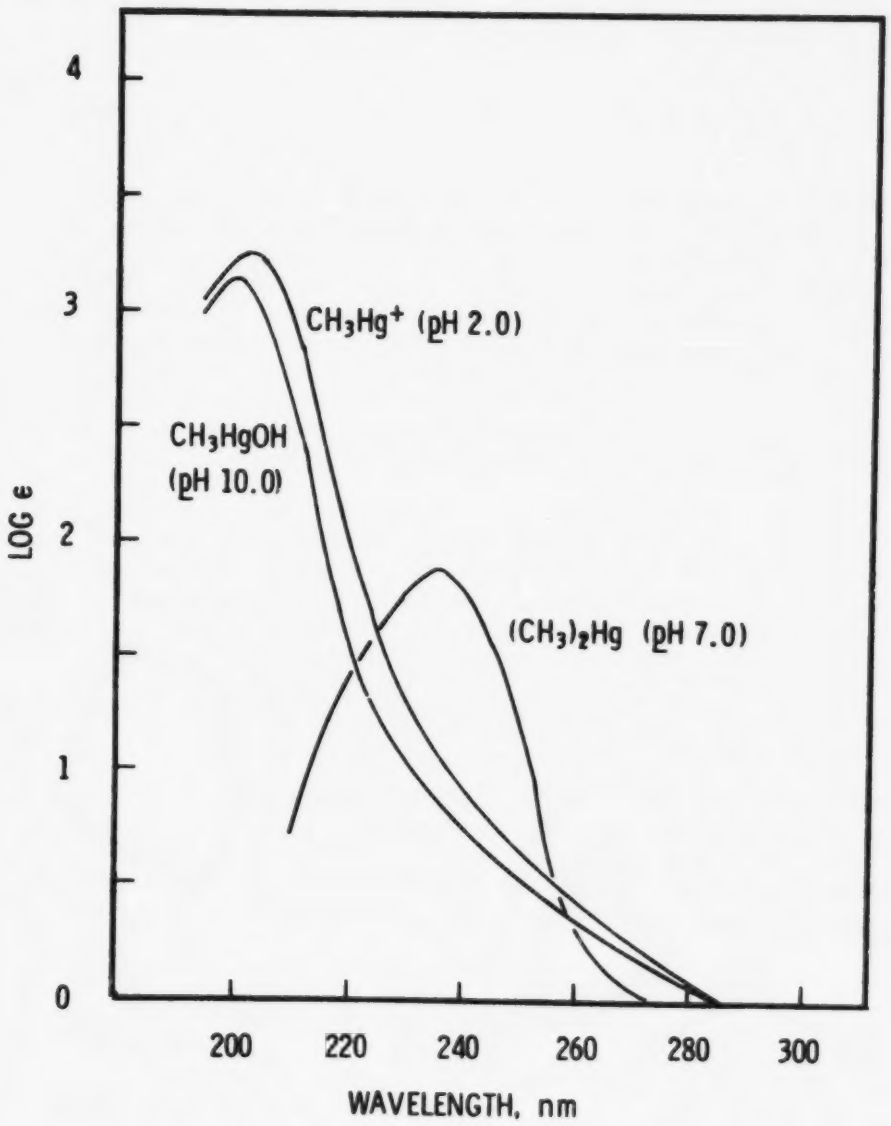


Figure 15. UV absorption spectra of dimethylmercury, methylmercuric ion, and methylmercuric hydroxide in water.

Table 10. EXPERIMENTAL PHOTOLYSIS RATES FOR FOUR METHYLMERCURY COMPOUNDS IN SUNLIGHT

Compound[a]	$10^3 (k_a)_{int} \phi$ hr^{-1}	$t_{\frac{1}{2}}$ hrs[b]
CH_3HgI	> 230	< 3
CH_3HgBr	6.2	110
CH_3HgCl	< 1.3	> 530
CH_3HgOH	< 1.3	> 530

[a] Concentration 1.00×10^{-4} M in water.
[b] Expressed in hours of sunlight, not actual hours.

Photoreactivity of Sulfur-bonded Methylmercury Complexes

As discussed earlier, under certain environmental conditions, a large fraction of the methylmercury species exists as sulfur-bonded methylmercury complexes. Earlier studies[88, 89] showed that mercuric mercaptides are readily decomposed by light from a mercury lamp or even ordinary room light.

Previously recorded ultraviolet spectra showed that some organomercuric mercaptides have significantly large extinction coefficients at wavelengths > 290 nm.[25] Methylmercuric sulfide ion, bis(methylmercuric) sulfide, and methylmercury-thiol complexes also absorb at wavelengths > 290 nm (Figures 16 and 17). Preliminary experiments showed that Pyrex-filtered ultraviolet light decomposed the sulfide and thiol complexes with cleavage of the methylmercury bond.

$$CH_3HgS^- \xrightarrow{h\nu} CH_4\uparrow + HgS\downarrow \qquad (45)$$

$$CH_3HgSR \xrightarrow{h\nu} CH_4\uparrow + C_2H_6\uparrow$$

$$+ \text{Inorganic mercury precipitate} \downarrow + RSSR \qquad (46)$$

Products of the photolyses were methane and ethane (20:1) gases and inorganic mercury precipitates. The black precipitate from photolysis of methylmercuric sulfide ion was found to be mercuric sulfide, and the precipitate from the methylmercury-thiol photolysis was not identified, but was shown by mass spectrometry to contain no organically bound mercury. Yields of inorganic mercury in the precipitates quantitatively accounted for disappearance of the methylmercury complexes. Under these same conditions, unphotolyzed controls formed no inorganic mercury during the photolysis period.

Disappearance quantum yields for photodegradation of several different methylmercury-thiol complexes by 313 nm light were similar (Table 11). Quantum yields for photodecomposition of the cysteine and egg albumin complexes are particularly significant, since these complexes are good models for methylmercury-thiol complexes that form in biological systems.[15, 90] In addition to complexation by sulfhydryl groups, the methylmercury ion was probably also complexed by other functional groups such as amino and hydroxyl groups in the albumin protein.[90] Such complexes would not be decomposed by 313 nm light, because methylmercury-nitrogen and methylmercury-oxygen complexes do not absorb light at wavelengths > 290 nm.[91]

Photodecomposition of the methylmercuric sulfide ion proceeded with a high quantum yield (Table 11). The complex was so light-sensitive that extensive photodegradation by fluorescent lights in the

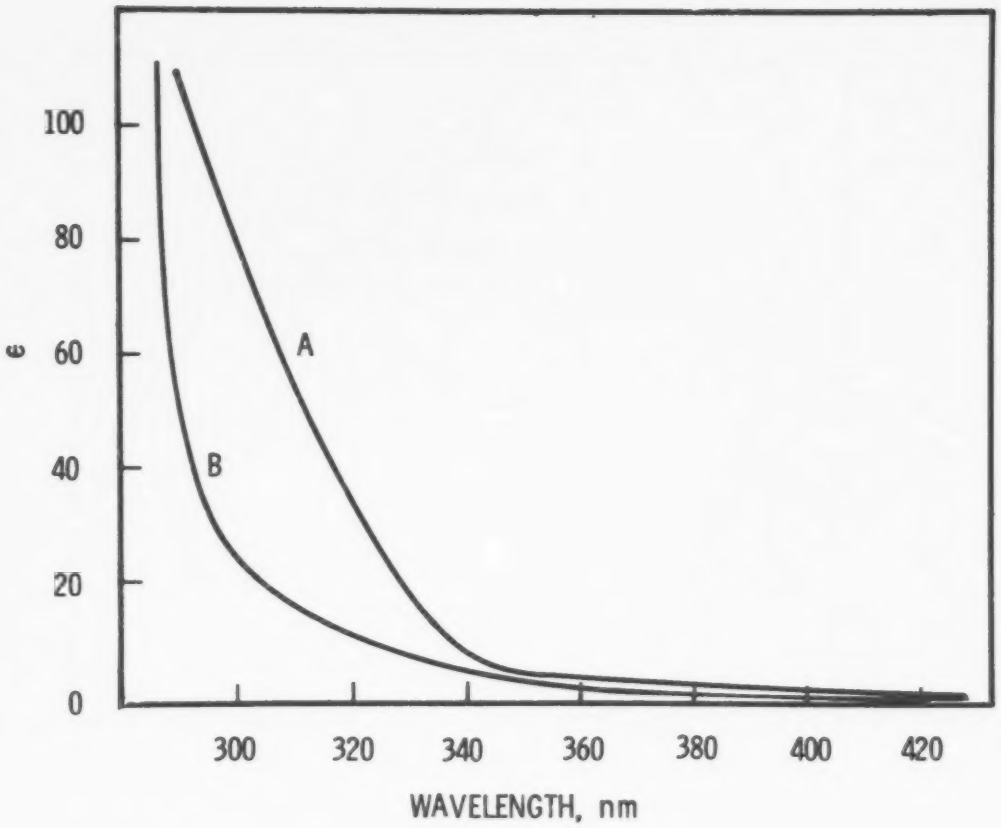


Figure 16. UV absorption spectra of methylmercuric sulfide ion (A) and bis(methylmercuric) sulfide (B).

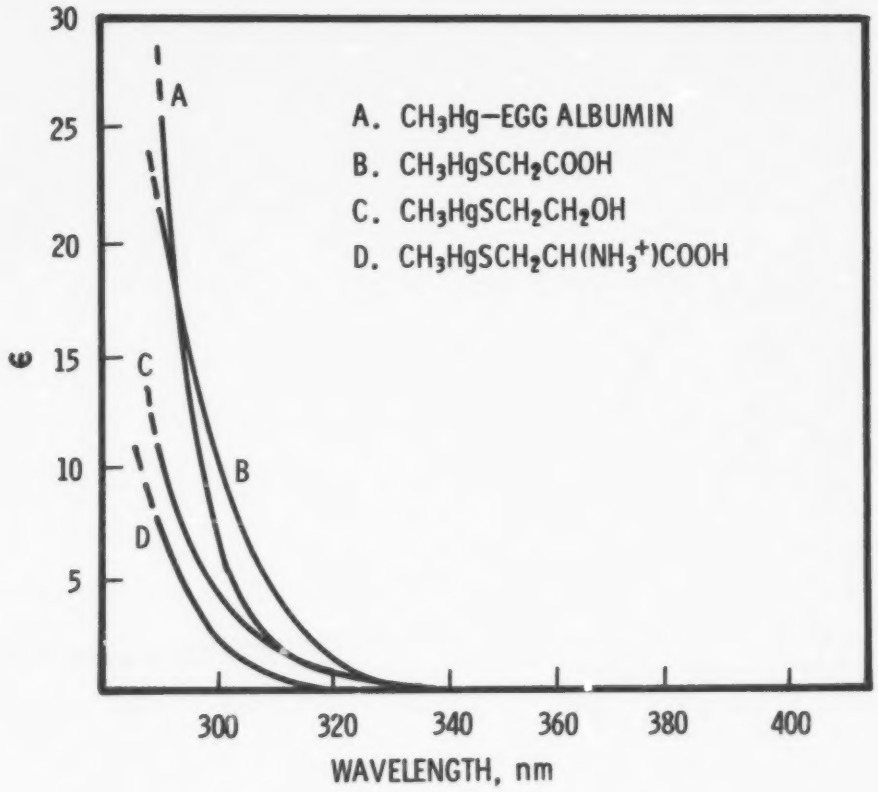


Figure 17. UV absorption spectra of methylmercury-thiol complexes.

Table 11. QUANTUM YIELDS FOR PHOTODEGRADATION OF SULFUR-BONDED METHYLMERCURY COMPLEXES AT 313 nm IN DISTILLED WATER

Complex	ϕ[a]
CH_3Hg-egg albumin	0.12 ± 0.02
$CH_3HgSCH_2CO_2H$	0.15 ± 0.01[b, c]
$CH_3HgSCH_2CH_2OH$	0.14 ± 0.01[b, c]
$CH_3HgSCH_2\dot{C}H(NH_3^+)CO_2H$	0.16 ± 0.02
CH_3HgS^-	0.65 ± 0.05[b]

[a] Disappearance quantum yield in degassed solutions.
[b] Quantum yield shown to be concentration independent.
[c] Quantum yield shown to be pH independent.

laboratory occurred over a period of a few days on the desk top. At high concentrations (0.10 M) with excess sulfide present, the complex was degraded by a dark reaction to form mercuric sulfide. This reaction was not investigated in detail because it proceeded at a much slower rate at concentrations < 0.01 M. Assuming second-order kinetics for the reaction, its rate constant was estimated to be $\sim 10^{-6}$ l/mole sec.

Photosensitization of the methylmercury-thioglycolic acid complex ($CH_3HgSCH_2CO_2H$) by acetone proceeded with about the same quantum yield (0.13) measured for the direct photolysis (0.15). Presumably, the other thiol complexes would undergo such sensitized photodecomposition also, since they all have the same structure about the mercury-sulfur chromophore. On the other hand, humic acid, a substance likely to be found in natural waters, did not photosensitize the decomposition of $CH_3HgSCH_2CO_2H$.

Quantum yields for photodecomposition of the methylmercury-thiol complexes were lowered by addition of quenchers (Table 12). Stern-Volmer plots (see eq 44) of the data were non-linear (Figure 18), indicating that two or more excited states are involved in the photodecomposition of the complexes.[92] Whatever the nature of the quenching processes, concentrations of quenchers such as oxygen are sufficiently high under certain environmental conditions to lower quantum yields for photodecomposition of the complexes. For example, the concentration of oxygen in air-saturated water ($\sim 3 \times 10^{-4}$ M) would lower the quantum yield for $CH_3HgSCH_2CH_2OH$ from 0.14 to 0.10.

Maximum rates of sunlight photodecomposition were calculated as described previously (Table 13) using quantum yields from Table 11 and spectral data from Figures 16 and 17. The rapid photolysis rate of the sulfide complex is due to the combination of its high quantum yield and large sunlight absorption rate constant. Since methylmercury ion is often complexed with sulfur-containing ligands in the environment, these data suggest that sunlight photodecomposition of sulfur-bonded methylmercury complexes plays an important role in the conversion of methylmercury to inorganic mercury compounds.

Photocleavage of Phenylmercury Compounds

Spectroscopic studies showed that phenylmercuric hydroxide, phenylmercury ion, and diphenylmercury (Figure 19) absorb at wavelengths > 290 nm. The absorption in this spectral region is due to singlet-triplet electronic transitions that have enhanced intensity because of perturbation by the heavy atom, mercury.[93,94] The singlet-triplet spectra of phenylmercuric ion and phenylmercuric hydroxide are identical. Thus, although changes in pH affect the composition of phenylmercuric species in aqueous solution (eq 47), the rate of sunlight absorption is pH-independent.

Table 12. EFFECT OF QUENCHERS UPON PHOTODECOMPOSITION OF SULFUR-BONDED METHYLMERCURY COMPLEXES IN WATER[a]

Complex	Quencher (Q)	10^3 [Q] M	ϕ_{Hg}[b]
$CH_3HgSCH_2CO_2H$	None	0	0.16
	2,4-hexadien-1-ol	86	0.063
	2,4-hexadien-1-ol	57	0.075
	2,4-hexadien-1-ol	38	0.082
	2,4-hexadien-1-ol	19	0.093
	sodium trans-cinnamate	20	0.085
	oxygen	1.4[c]	0.075
$CH_3HgSCH_2CH_2OH$	None	0	0.14
	2,4-hexadien-1-ol	39	0.043
	2,4-hexadien-1-ol	4.9	0.046
	2,4-hexadien-1-ol	0.49	0.087
CH_3HgS^-	None	0	0.65
	Oxygen	1.4[c]	0.08

[a] Quenching studies carried out at 313 nm under conditions in which no light absorbed by quencher.
[b] Quantum yield for formation of inorganic mercury.
[c] Oxygen-saturated water.

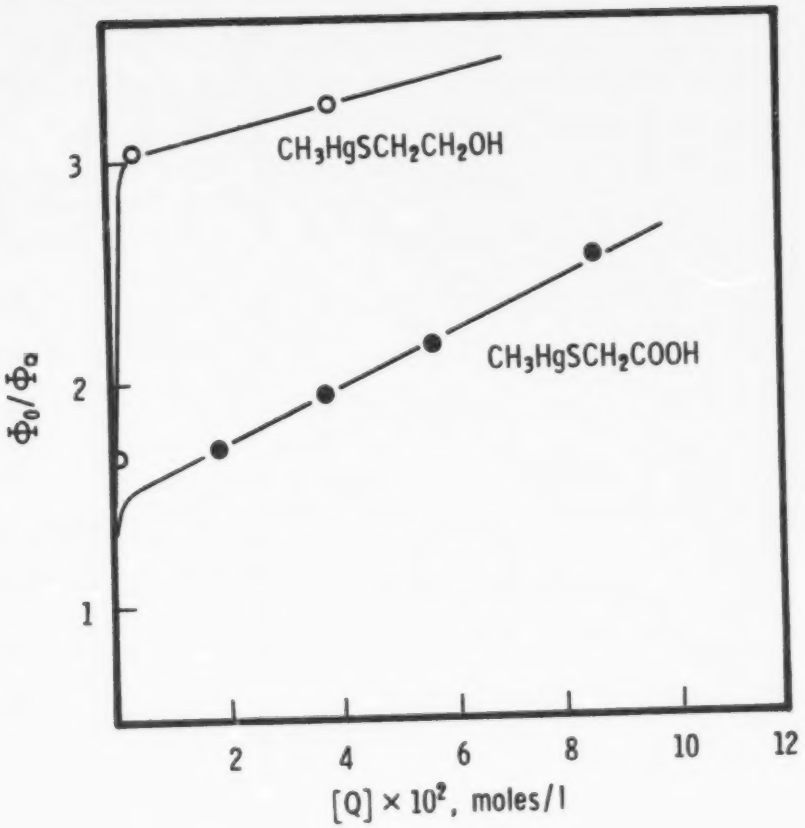


Figure 18. Effect of quencher, 2,4-hexadien-1-ol, upon quantum yields for photocleavage of methylmercury-thiol complexes.

Table 13. CALCULATED SUNLIGHT PHOTOLYSIS RATES FOR SULFUR-BONDED METHYLMERCURY COMPLEXES AT 25° IN WATER

Complex	10^2 $(k_s)_{int}$ hr^{-1}	10^3 $\phi(k_s)_{int}$ hr^{-1}	$t_{\frac{1}{2}}$ hr
CH_3Hg-egg albumin	10	12	58
$CH_3HgSCH_2CO_2H$	10	15	46
$CH_3HgSCH_2CH_2OH$	11	15	46
$CH_3HgSCH_2CH(NH_3^+)CO_2H$	3.6	5.8	120
CH_3HgS^-	240	1600	0.43

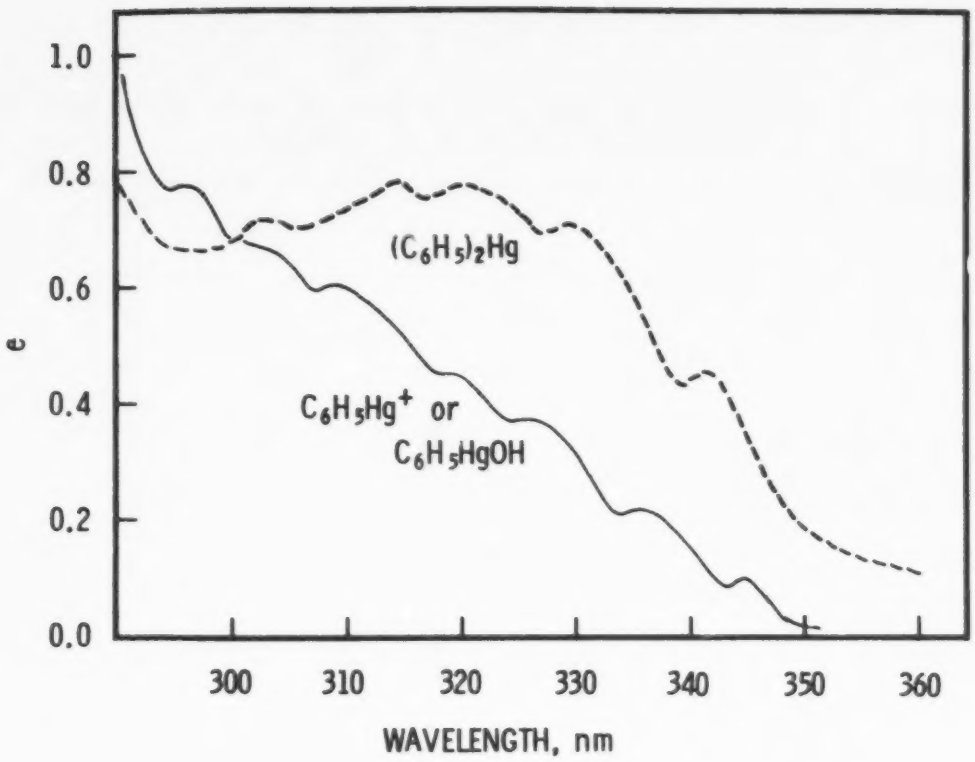


Figure 19. UV absorption spectra of phenylmercury compounds.

$$C_6H_5Hg^+ + H_2O \overset{K}{\rightleftharpoons} C_6H_5HgOH + H^+ \quad (47)$$

$K = 6.8 \times 10^{-5}$ (Reference 16)

Irradiation of diphenylmercury, phenylmercuric hydroxide, and phenylmercury ion in degassed solutions caused the following reactions:

$$(C_6H_5)_2Hg \xrightarrow{h\nu} C_6H_5Hg\cdot + C_6H_5\cdot \quad (48)$$

$$C_6H_5Hg\cdot \rightarrow C_6H_5\cdot + Hg^\circ\downarrow \quad (49)$$

$$C_6H_5Hg^+ \xrightarrow{h\nu} C_6H_5\cdot + \cdot Hg^+ \quad (50)$$

$$2\cdot Hg^+ \rightarrow Hg_2^{2+} \quad (51)$$

$$C_6H_5HgOH \xrightarrow{h\nu} C_6H_5\cdot + \cdot HgOH \quad (52)$$

$$2\cdot HgOH \rightarrow Hg_2(OH)_2 \quad (53)$$

$$Hg_2(OH)_2 \rightarrow HgO\downarrow + Hg^\circ\downarrow + H_2O \quad (54)$$

$$C_6H_5\cdot + RH \rightarrow C_6H_6 + R\cdot \quad (55)$$

$$2C_6H_5\cdot \rightarrow (C_6H_5)_2\downarrow \quad (56)$$

Quantitative yields of metallic mercury and phenyl free radicals resulted from irradiation of diphenylmercury. Phenylmercuric ion photolyzed to give phenyl radicals and mercurous ions, and phenylmercuric hydroxide yielded phenyl radicals and nearly quantitative yields of metallic mercury and yellow mercuric oxide. The fate of the phenyl radicals depended upon the composition of the reaction media. With organic materials (RH) present in the aqueous media, phenyl radicals reacted to form nearly quantitative yields of benzene (eq 55). In oxygen free distilled water containing no additional organic substances, the most important phenyl radical reaction was coupling to form biphenyl (eq 56). With oxygen present, no biphenyl was formed, presumably because the phenyl radicals were scavenged by the following reaction.

$$C_6H_5\cdot + O_2 \rightarrow C_6H_5O_2\cdot \quad (57)$$

Previous studies by Russell and Bridger have shown that reaction 57 occurs much more rapidly than reaction 56 in cyclohexane and carbon tetrachloride.[95] Products that resulted from reactions of the phenylperoxy radical were not identified because of their complexity.

Disappearance quantum yields for photodecomposition of the phenylmercury compounds with 313 nm light are summarized in Table 14. Phenylmercuric perchlorate was used in the study because it is completely dissociated in water at the high concentrations used in the experiments. At pH 2.3 and pH 10.3, the phenylmercuric species existed as phenylmercuric ion and phenylmercuric hydroxide, respectively (eq 47). However, results in Table 14 show that the quantum yield for photodegradation of phenylmercuric salts is the same at both pH's. Because the broad-band (> 290 nm) quantum yield for disappearance of phenylmercuric perchlorate (0.23 ± 0.03) was about the same as the 313-nm quantum yield, the quantum yield was assumed to be wavelength-independent. Benzene (0.80 moles per mole of phenylmercury compound decomposed) and inorganic mercury containing precipitates were formed at both pH values in the acetone-sensitized studies.

Photodecomposition of phenylmercurials was sensitized efficiently by acetone (triplet energy 80 kcal/mole), but not by sensitizers with triplet energies < 74 kcal/mole (Table 15). The triplet-state energy of phenylmercurials must therefore be between 74 and 80 kcal/mole, because efficient photosensitization occurs only when the sensitizer triplet energy is equal to or greater than that of the photoreactive compound.[96] Ultraviolet absorption spectra of the phenylmercury compounds (Figure 19) show that their triplet energies are $\sim$ 80 kcal/mole. The similarity of quantum yields in the direct and sensitized photolyses is not surprising since both involve excitation of the phenylmercury compounds to their triplet states.

Photosensitized conversion of phenylmercury to inorganic mercury compounds is unlikely to be generally important in the aquatic environment for the following reasons:

- Most compounds with triplet energies $\geq$ 80 kcal mole^{-1} do not absorb strongly at wavelengths > 290 nm.

- Observed concentrations of mercury compounds in natural waters are generally very low ($< 10^{-9}$ M). Because much higher concentrations of competing energy acceptors, such as oxygen, are usually present in the environment, photosensitization would be negligible.

Stern-Volmer plots for the quenching of diphenylmercury photodecomposition were linear (Figure 20). In acetonitrile, the slope of the plot, $k_q \tau$, was only 0.20. Assuming a value of 1.0×10^{10} ℓ/mole sec for k_q in acetonitrile,[97] the indicated triplet lifetime,

Table 14. QUANTUM YIELDS FOR DIRECT PHOTOLYSIS (313 nm) OF PHENYLMERCURY COMPOUNDS

Compound	Solvent	Disappearance Quantum Yield
$(C_6H_5)_2Hg$	Benzene	0.33 ± 0.01
$(C_6H_5)_2Hg$	Acetonitrile	0.40 ± 0.02
$(C_6H_5)_2Hg$	Water, pH 7.0	0.27 ± 0.02[a]
$C_6H_5HgClO_4$	Water, pH 2.3	0.25 ± 0.02
$C_6H_5HgClO_4$	Water, pH 10.3	0.24 ± 0.02

[a] Extrapolated using viscosity data.

Table 15. QUANTUM YIELDS FOR PHOTOSENSITIZATION OF PHENYLMERCURIALS

Compound	Sensitizer	Triplet Energy (kcal $mole^{-1}$)	Solvent	Disappearance Quantum Yield
$(C_6H_5)_2Hg$	Acetone	80	Benzene	0.33
$(C_6H_5)_2Hg$	Acetophenone	74	Benzene	< 0.003
$(C_6H_5)_2Hg$	Benzophenone	68	Benzene	< 0.006
$(C_6H_5)_2Hg$	Naphthalene	62	Benzene	0.027
$(C_6H_5)_2Hg$	Anthracene	42	Benzene	< 0.003
$C_6H_5HgO_2CCH_3$	Acetone	80	Water, pH 4.0	0.23
$C_6H_5HgClO_4$	Acetone	80	Water, pH 2.3	0.23

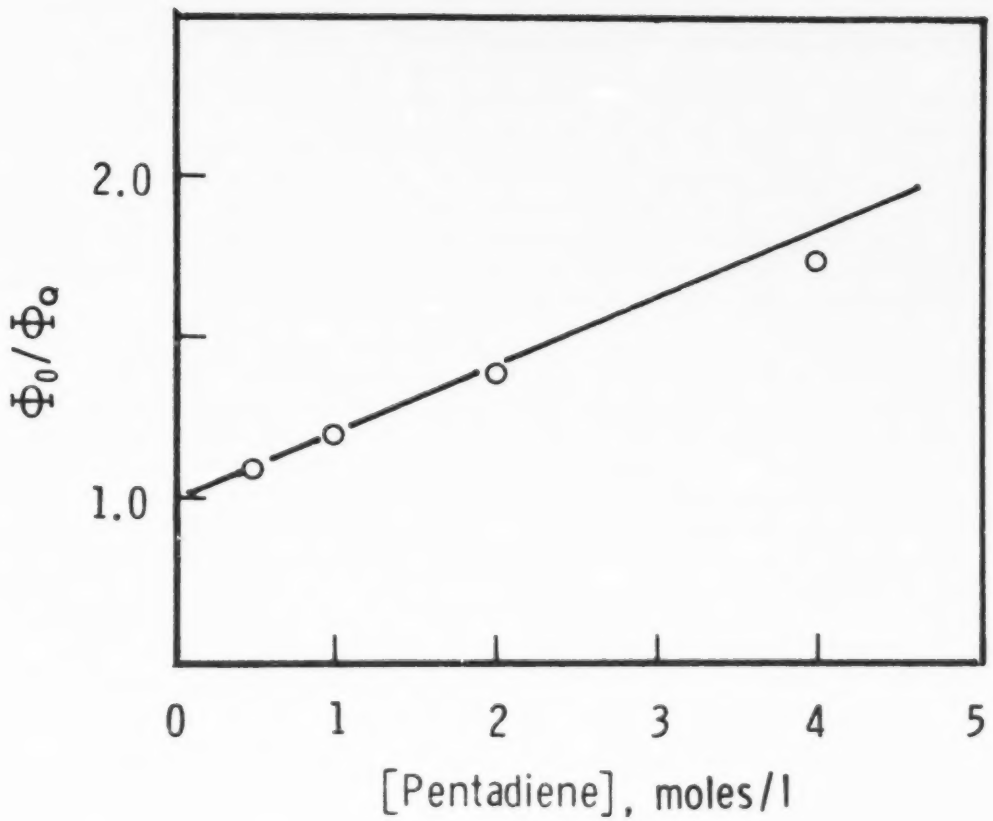


Figure 20. Quenching of diphenylmercury photolysis by cis-1,3-pentadiene in acetonitrile.

τ, for diphenylmercury is 2.0×10^{-11} sec. Disappearance quantum yields in water for phenylmercury ion and phenylmercuric hydroxide were not decreased by quencher concentrations less than 0.10 M, indicating that τ for these compounds is $< 10^{-10}$ sec. Because concentrations of potential quenchers in natural waters are much lower than 0.1 M, quantum yields in Table 14 should be unaffected by quenching processes in the environment.

To determine empirically the effect of materials dissolved in natural waters on the quantum yield for photodecomposition of a phenylmercuric salt, air-saturated solutions of phenylmercuric acetate (1.0×10^{-3} M) in two different natural waters and in distilled water were subjected to equal exposures of Pyrex-filtered mercury-lamp light (> 290 nm). The phenylmercuric salt photodecomposed at the same rate in all three solutions, in agreement with the predictions derived from the quenching studies. Dark controls showed no decomposition.

Sunlight photolysis rates calculated from laboratory data and photolysis rates measured in sunlight are compared in Table 16. Other experiments showed that the same salts were completely decomposed after 18 days in sunlight while dark controls showed no change. With the exception of diphenylmercury, the compounds were largely dissociated and hydrolyzed to form 25% phenylmercuric ion and 75% phenylmercuric hydroxide under the experimental conditions. Results in Table 16 show that the calculated and empirical photolysis rates are in reasonable agreement.

Table 16. COMPARISON OF CALCULATED AND EMPIRICAL RATES FOR PHOTODEGRADATION OF PHENYLMERCURY COMPOUNDS IN SUNLIGHT

Compound	Calculated $10^2 (k_a)_{int} \phi$, hr^{-1} [a]	Empirical $10^2 (k_a)_{int} \phi$ [b, c]	Empirical $t_{1/2}$ hrs
$(C_6H_5)_2Hg$		8.1 ± 1.7	8.5 ± 1.8
$C_6H_5HgOCOCH_3$	3.3	4.3 ± 0.3	16.0 ± 2
$C_6H_5HgNO_3$	3.3	3.5 ± 0.2	20.0 ± 1
$C_6H_5HgBO_3$	3.3	5.0 ± 0.3	14.0 ± 2
C_6H_5HgOH	3.3	4.3 ± 0.3	16.0 ± 2

[a] Calculated from solar radiation data, extinction coefficients, and quantum yields in Table 14.
[b] Average of three replicates irradiated by sunlight.
[c] Calculated assuming first-order kinetics for photodecomposition.

SECTION VII

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SECTION VIII

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SECTION IX

APPENDICES

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APPENDIX A

METHYLMERCURIC ION EQUILIBRIUM CALCULATIONS

The total concentration of methylmercury species present in a system was represented as the sum of the concentrations of all complexes incorporating the methylmercury moiety, plus the concentration of the free ion itself. The formation constant expressions for the various complexes considered were solved for the concentration of the complex. Substitution of the concentration expression so derived into the methylmercury concentration equation yielded an equation for $\Sigma[CH_3Hg]$ as a function of any one methylmercury complex. Dividing both sides by the concentration of the complex and rearranging terms yields an expression for the fraction of the total methylmercury that exists as a given complex. Because the formation constant for bis(methylmercury) sulfide contains a squared term, the resulting expression is second-order and requires an iterative technique for solution.

An example has been worked out in detail for the complexing agents, OH^-, Cl^-, $S^=$, thiol (RSH), amino nitrogen (RNH_2), ammonia, humic acids (ArOH), and orthophosphate. The formation constants (Appendix B) indicate that few other complexes are likely to be important in the environment, so other complexing agents were excluded from the sample calculation.

The total concentration of methylmercury in the system is expressed as:

$$\Sigma[CH_3Hg] = [CH_3HgS^-] + [CH_3HgOH] + 2[(CH_3Hg)_2S]$$

$$+ [CH_3HgCl] + [CH_3HgNH_2R^+] + [CH_3HgSR] + [CH_3HgHPO_4^-]$$

$$+ [CH_3HgNH_3^+] + [CH_3HgOAr] + [CH_3Hg^+] \qquad (58)$$

The following formation equilibrium expressions and the constants (Appendix B) were then solved for the concentration of the respective complexes.

$$CH_3Hg^+ + S^= \overset{K_1}{\rightleftharpoons} CH_3HgS^-$$

$$K_1 = \frac{[CH_3HgS^-]}{[CH_3Hg^+]\,[S^=]} = 10^{21.2}$$

$$CH_3Hg^+ + OH^- \overset{K_2}{\rightleftharpoons} CH_3HgOH$$

$$K_2 = \frac{[CH_3HgOH]}{[CH_3Hg^+]\,[OH^-]} = 10^{9.37}$$

$$CH_3Hg^+ + CH_3HgS^- \overset{K_3}{\rightleftharpoons} (CH_3Hg)_2S$$

$$K_3 = \frac{[(CH_3Hg)_2S]}{[CH_3Hg^+]\,[CH_3HgS^-]} = 10^{16.3}$$

$$CH_3Hg^+ + Cl^- \overset{K_4}{\rightleftharpoons} CH_3HgCl$$

$$K_4 = \frac{[CH_3HgCl]}{[CH_3Hg^+]\,[Cl^-]} = 10^{5.25}$$

$$CH_3Hg^+ + RNH_2 \overset{K_5}{\rightleftharpoons} RNH_2HgCH_3^+$$

$$K_5 = \frac{[RNH_2HgCH_3^+]}{[RNH_2]\,[CH_3Hg^+]} = 10^{8.25}$$

$$CH_3Hg^+ + SR^- \overset{K_6}{\rightleftharpoons} CH_3HgSR$$

$$K_6 = \frac{[CH_3HgSR]}{[CH_3Hg^+]\,[SR^-]} = 10^{16.12}$$

$$CH_3Hg^+ + HPO_4^{2-} \overset{K_7}{\rightleftharpoons} CH_3HgHPO_4^-$$

$$K_7 = \frac{[CH_3HgHPO_4^-]}{[CH_3Hg^+]\,[HPO_4^{2-}]} = 10^{5.03}$$

$$CH_3Hg^+ + NH_3 \overset{K_8}{\rightleftharpoons} CH_3HgNH_3^+$$

$$K_8 = \frac{[CH_3HgNH_3^+]}{[CH_3Hg^+]\,[NH_3]} = 10^{7.60}$$

$$CH_3Hg^+ + ArO^- \overset{K_9}{\rightleftharpoons} CH_3HgOAr$$

$$K_9 = \frac{[CH_3HgOAr]}{[CH_3Hg^+]\,[ArO^-]} = 10^{6.5}$$

Substitution of the above in equation 58 and division of both sides by $[CH_3HgS^-]$ gives the following equation:

$$\frac{\Sigma[CH_3Hg]}{[CH_3HgS^-]} = 1 + \frac{K_2}{K_1}\frac{[OH^-]}{[S^=]} + \frac{2K_3}{K_1}\frac{[CH_3HgS^-]}{[S^=]}$$

$$+ \frac{K_4}{K_1}\frac{[Cl^-]}{[S^=]} + \frac{K_5}{K_1}\frac{[RNH_2]}{[S^=]} + \frac{K_6}{K_1}\frac{[SR^-]}{[S^=]} + \frac{K_7}{K_1}\frac{[HPO_4^{2-}]}{[S^=]}$$

$$+ \frac{K_8}{K_1}\frac{[NH_3]}{[S^=]} + \frac{K_9}{K_1}\frac{[ArO^-]}{[S^=]} + \frac{1}{K_1[S^=]} \qquad (59)$$

Simplifying and taking the reciprocal of both sides gives the fraction of methylmercury existing as CH_3HgS^-.

$$\frac{[CH_3HgS^-]}{\Sigma\,[CH_3Hg]} =$$

$$\frac{K_1[S^=]}{K_1[S^=] + K_2[OH^-] + 2K_3[CH_3HgS^-] + K_4[Cl^-] + K_5[RNH_2] + K_6[SR^-]}$$

$$+ K_7[HPO_4^{2-}] + K_8[NH_3] + K_9[ArO^-] + 1 \qquad (60)$$

The concentrations of $[S^=]$, $[RNH_2]$, $[RS^-]$, $[HPO_4^{2-}]$, $[NH_3]$, and $[ArO^-]$ are difficult to measure and are also pH-dependent; they must therefore be defined in terms of more easily measurable variables. Equations 67-72 redefine the variables in terms of quantities that can be more readily estimated.

$$\Sigma S = [H_2S] + [S^{=}] + [SH^{-}] \quad (61)$$

$$\Sigma RN = [RNH_2] + [RNH_3^{+}] \quad (62)$$

$$\Sigma RS = [RS^{-}] + [RSH] \quad (63)$$

$$\Sigma PO_4 = [H_2PO_4^{-}] + [HPO_4^{2-}] \quad (64)$$

$$\Sigma N = [NH_3] + [NH_4^{+}] \quad (65)$$

$$\Sigma ArO = [ArOH] + [ArO^{-}] \quad (66)$$

Substituting expressions for acid-base equilibria into equations 61-66 and rearranging terms results in the following:

$$[S^{=}] = \frac{6.3\Sigma S}{10^{22}[H^{+}]^2 + 10^{15}[H^{+}] + 6.3} \quad (67)$$

$$[RNH_2] = \frac{\Sigma RN}{1 + K_n\,[H^{+}]} \qquad K_n = 10^{10} \quad (68)$$

$$[RS^{-}] = \frac{\Sigma RS}{1 + K_s\,[H^{+}]} \qquad K_s = 10^{9.52} \quad (69)$$

$$[HPO_4^{2-}] = \frac{\Sigma PO_4}{1 + K_p\,[H^{+}]} \qquad K_p = 10^{6.79} \quad (70)$$

$$[NH_3] = \frac{\Sigma N}{1 + K_a\,[H^{+}]} \qquad K_a = 10^{9.42} \quad (71)$$

$$[ArO^{-}] = \frac{\Sigma ArO}{1 + K_h\,[H^{+}]} \qquad K_h = 10^{9.8} \quad (72)$$

where K_n, K_s, K_p, K_a, and K_h are equilibrium constants for protonation of amino acids, thiolate ions, hydrogen phosphate, ammonia, and phenolate ions, respectively.

The final solution is obtained by substituting equations 67-72 into equation 60, eliminating the $[OH^-]$ term, and rearranging to give

$$\frac{[CH_3HgS^-]}{\Sigma[CH_3Hg]} = \frac{K_1\,[S^=]}{X + K_1\,[S^=]} \tag{73}$$

where $X = 1 + \frac{K_w K_2}{[H^+]} + 2K_3\,[CH_3HgS^-] + K_4\,[Cl^-] + \frac{K_5 \Sigma RN}{1 + K_n\,[H^+]}$

$$+ \frac{K_6 \Sigma RS}{1 + K_s\,[H^+]} + \frac{K_7 \Sigma PO_4}{1 + K_p\,[H^+]} + \frac{K_8 \Sigma N}{1 + K_a\,[H^+]} + \frac{K_9 \Sigma ArO}{1 + K_h\,[H^+]}$$

and K_w represents the ionization constant of water.

Using similar procedures, the fraction of methylmercury existing as $(CH_3Hg)_2S$ was derived (eq 74).

$$\frac{2\,[(CH_3Hg)_2S]}{\Sigma[CH_3Hg]} = \frac{2K_{10}\,[CH_3HgS^-]^2}{[S^=]\,\Sigma[CH_3Hg]} \tag{74}$$

$$K_{10} = \frac{[(CH_3Hg)_2S]\,[S^=]}{[CH_3HgS^-]^2} = 10^{-4.9} \tag{75}$$

Expressions derived for the relative concentrations of other methylmercury complexes are shown below.

Where $F3 = \frac{[CH_3Hg^+]}{\Sigma\,[CH_3Hg]} = \frac{1}{X + K_1\,[S^=]}$ (76)

$$\frac{[CH_3HgCl]}{\Sigma\,[CH_3Hg]} = K_4\,[Cl^-]\,(F3) \tag{77}$$

$$\frac{[CH_3HgNH_2R^+]}{\Sigma\,[CH_3Hg]} = \frac{K_5\,(\Sigma RN)\,(F3)}{1 + K_n\,[H^+]} \tag{78}$$

$$\frac{[CH_3HgSR]}{\Sigma\,[CH_3Hg]} = \frac{K_6\ (F3)\ \Sigma RS}{1 + K_s\ [H^+]} \tag{79}$$

$$\frac{[CH_3HgOH]}{\Sigma\,[CH_3Hg]} = \frac{K_2\ (F3)\ K_w}{[H^+]} \tag{80}$$

$$\frac{[CH_3HgHPO_4^-]}{\Sigma\,[CH_3Hg]} = \frac{K_7\ (F3)\ \Sigma PO_4}{1 + K_p\ [H^+]} \tag{81}$$

$$\frac{[CH_3HgNH_3^+]}{\Sigma\,[CH_3Hg]} = \frac{K_8\ (F3)\ \Sigma N}{1 + K_n\ [H^+]} \tag{82}$$

$$\frac{[CH_3HgOAr]}{\Sigma\,[CH_3Hg]} = \frac{K_9\ (F3)\ \Sigma ArO}{1 + K_h\ [H^+]} \tag{83}$$

The computer program used for the calculations is shown in Figure 1A. Originally developed as a Conversational Programming System (CPS) program, it was later converted to Fortran IV for plotting of the calculated fractions. Calculations were carried out on an IBM 360/67 computer. Calculations from the latter were plotted on a Tektronix 4010-1 terminal. Typical computer plots are shown on the following pages (Figures 2A-7A). Concentrations of all chemical species used in the calculations, except sulfur compounds, are given below.

$\Sigma\,[CH_3Hg] = 10^{-10}$ M

$\Sigma\,RN = 10^{-6}$ M

$\Sigma\,PO_4 = 10^{-6}$ M

$\Sigma\,N = 10^{-5}$ M

$\Sigma\,ArO = 10^{-5}$ M

$[Cl^-] = 10^{-4}$ M

```
X
?LOGIN(SEWL,GENERAL)
PASSWORD:
*******
GOOD AFTERNOON; USER IS; TIME  12:32:55  4/05/73;
?LOAD (MEMGFR)
?LIST
    1.      B1:     GET LIST(C1,C2,C3,C4,C5,C9,C10,C11);
    1.1             GET LIST(HB,LAST,DELT,X);
    2.              PUT LIST(' ');
    3.              PUT LIST('(H2S)+(SH-)+(S=)=',C1);
    3.1             PUT LIST('(H2PO4-)+(HPO4=)=',C9);
    4.              PUT LIST('(CL-)=',C2);
    4.1             PUT LIST('(NH4+)+(NH3)=',C10);
    4.2             PUT LIST('(AROH)+(ARO-)=',C11);
    5.              PUT LIST('(RNH3+)+(RNH2)=',C3);
    6.              PUT LIST('(ROH)+(RO-)=',C4);
    7.              PUT LIST('TOTAL MEMG CONC=' C5);
    8.              PUT LIST(' ');
    9.              C6=HB;
   10.              DO HUH=1 TO LAST; ↩
   11.              PUT LIST('PH=',LOG10(1/C6));
   12.              PUT LIST(' ');
   14.              C8=.1E-10;
   15.              C7=6.3*C5/(.1E23*C6**2+.1E16*C6+6.3);
   16.              PUT LIST('(S=)=',C7);
   17.              IF C7=0 THEN C8=0;
   20.              Z=1+10**-4.63/C6+10**5.25*C2;
   21.              Z1=10**8.25*C3/(1+10**10*C6)+10**16.12*C4/(1+10**9.52*C
);
                                                    6
   22.              Z2=10**5.03*C9/(1+10**6.79*C6)+10**7.6*C10/(1+10**9.42*
6);
                                                  C
   23.              Z4=10**6.5*C11/(1+10**9.8*C6);
   25.      IT:     Z3=Z+Z1+Z2+Z4+2*10**16.3*C8;
   30.              F1=10**21.2*C7/(Z3+10**21.2*C7);
   35.              C8P=F1*C5;
   36.              IF F1=0 THEN GO TO B2;
   37.              IF ABS((C8-C8P)/C8)<DELT THEN GO TO COMP;
   40.              C8=EXP((LOG(C8)+LOG(C8P))/2);
   45.              GO TO IT;
   50.      COMP:   F2=2*10**-4.9*C8**2/(C7*C5);
   55.      B2:     F3=1/(Z+Z1+Z2+Z4+10**21.2*C7+2*10**16.3*C8);
   56.              F7=10**9.37*F3*.1E-13/C6;
   57.              F9=10**5.03*F3*C9/(1+10**6.79*C6);
   58.              F10=10**7.6*F3*C10/(1+10**9.42*C6);
   59.              IF F1=0 THEN F2=0;
   60.              F4=10**5.25*C2*F3;
   65.              F5=10**5.25*C3*F3/(1+.1E11*C6);
   66.              F11=10**6.5*F3*C11/(1+10**9.5*C6);
   70.              F6=10**16.12*F3*C4/(1+10**9.52*C6);
   71.              F8=F1+F2+F3+F4+F5+F6+F7+F9+F10+F11;
   75.              PUT LIST('FRACTION MEMGS=',F1);
   80.              PUT LIST('FRACTION DISMEMGS=',F2);
   85.              PUT LIST('FRACTION MEMG+=',F3);
   86.              PUT LIST('FRACTION MEMGOH=',F7);
   87.              PUT LIST('FRACTION MEMGHPO4=',F9);
   88.              PUT LIST('FRACTION MEMGNH3=',F10);
   90.              PUT LIST('FRACTION MEMGCL=',F4);
   91.              PUT LIST('FRACTION MEMGOAR=',F11);
   95.              PUT LIST('FRACTION MEMGH2IR=',F5);
  100.              PUT LIST('FRACTION MEMGSP=',F6);
  101.              PUT LIST('SUM OF FRACTIONS=',F8);
  102.              PUT LIST(' ');
  103.              PUT LIST(' ');
  104.              C6=C6*10**X;
  105.              END ;
  110.              GO TO B1;
?LOGOU;
TIME 12:39:12; TIME USED: CPU 00:00:05; TERM 00:06:18; PAGE 00:05:36;
```

Figure A1. Computer program used for calculations in Appendix A.

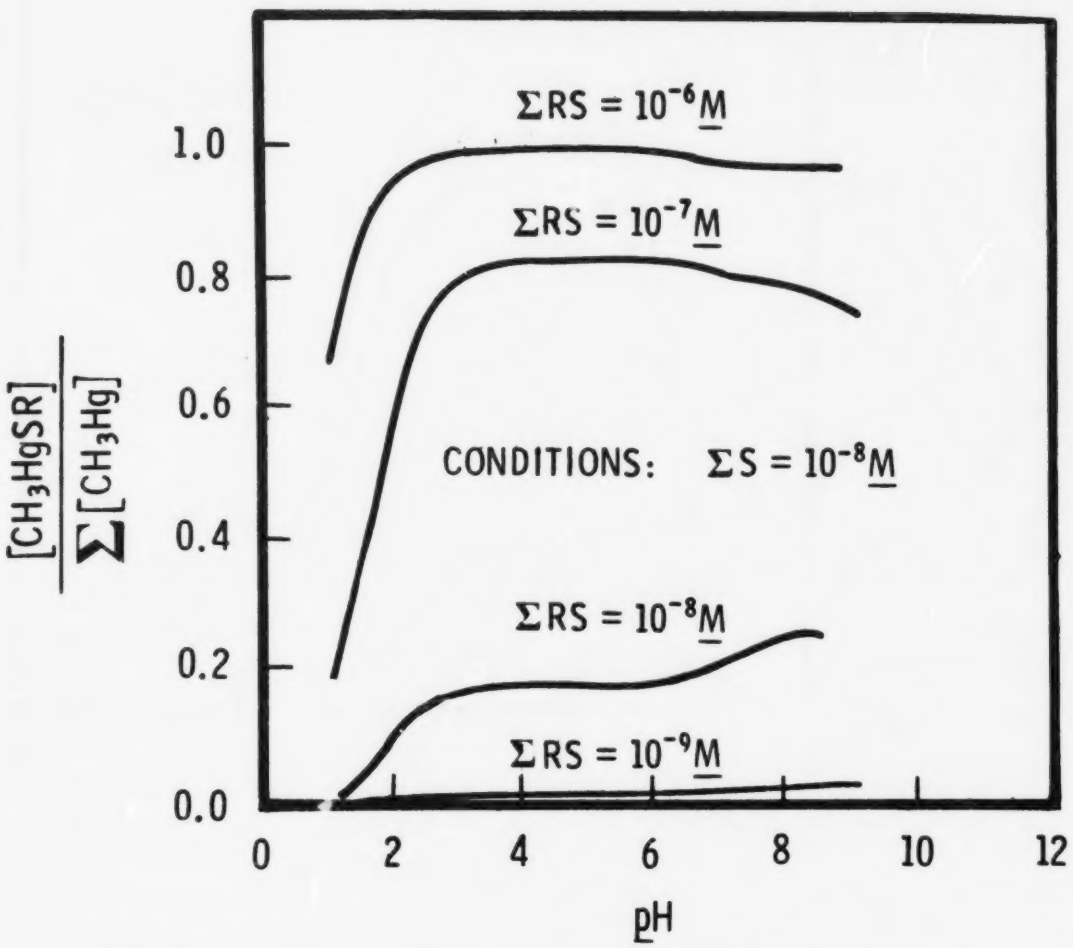

Figure A2. Relative concentrations of methylmercuric-thiol complexes in systems containing a low concentration of reduced sulfur species.

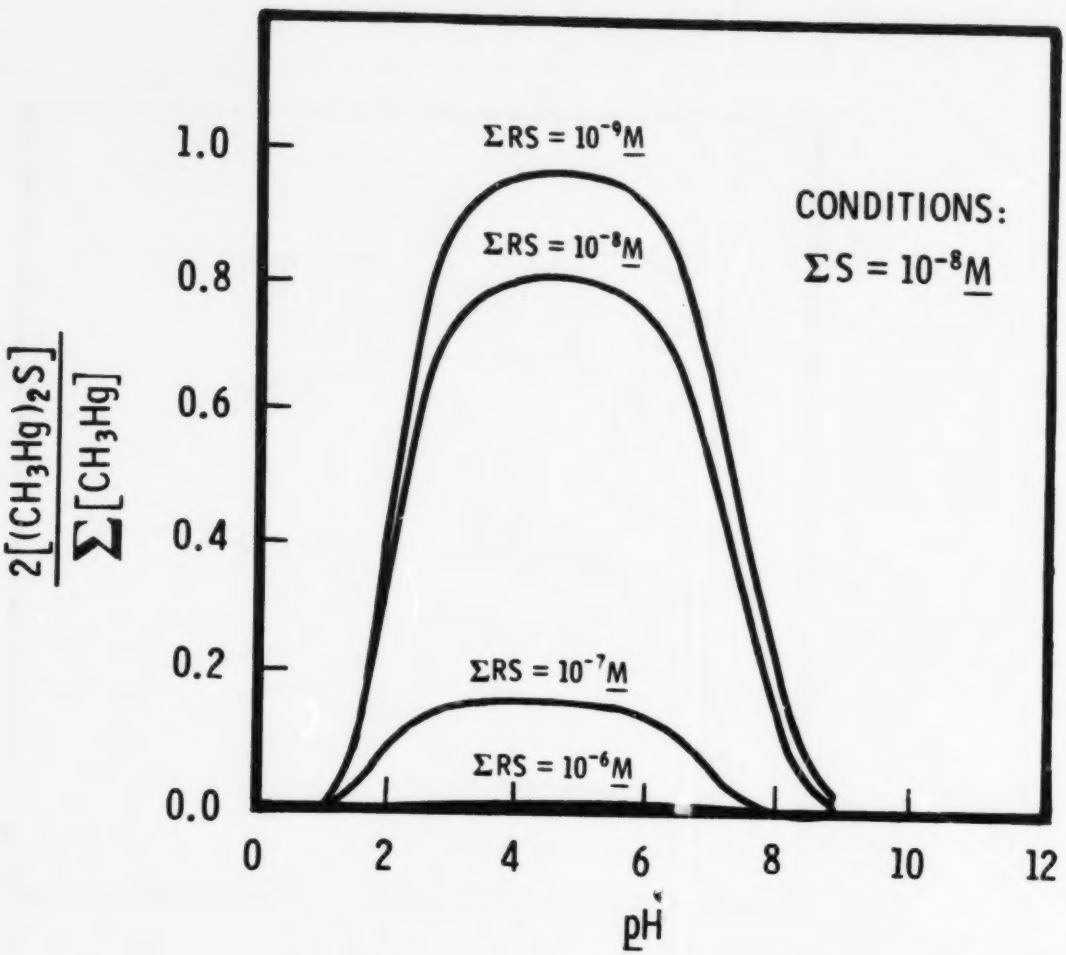

Figure A3. Relative concentrations of $(CH_3Hg)_2S$ in systems containing a low concentration of reduced sulfur species.

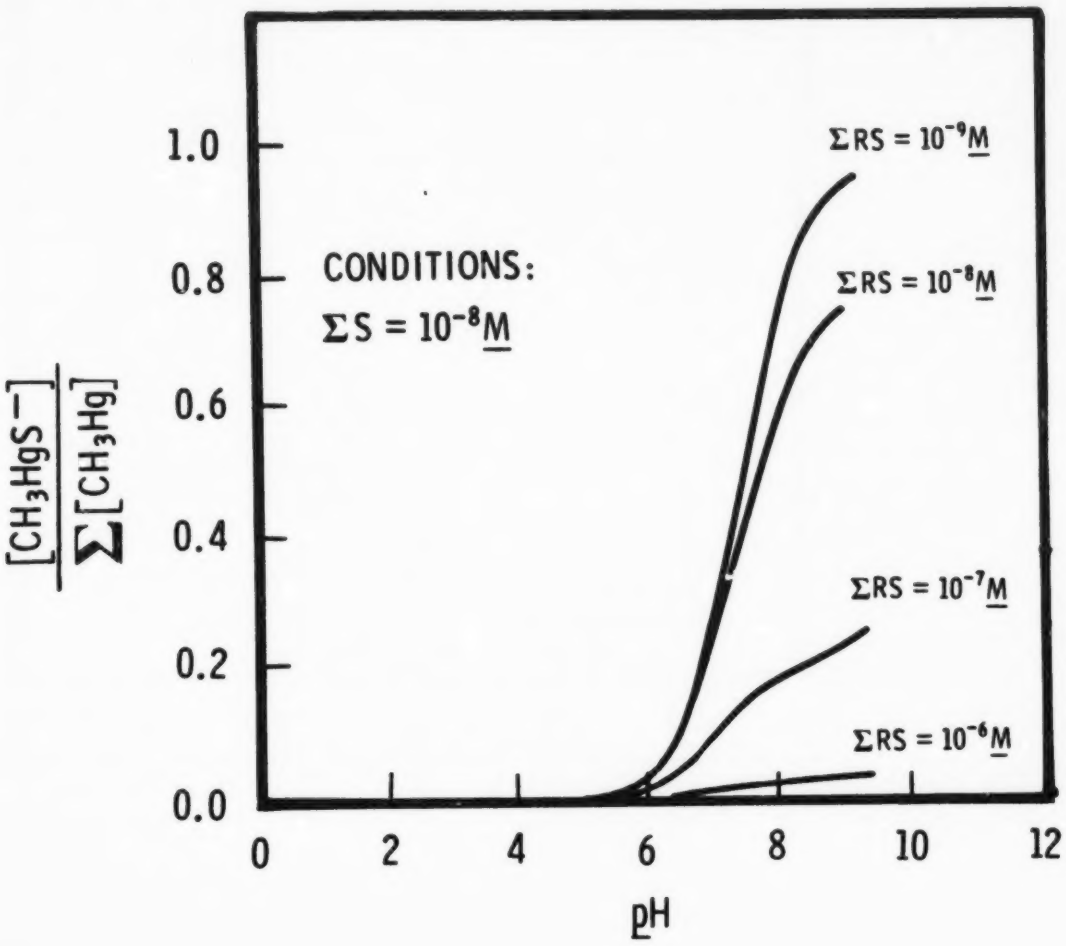

Figure A4. Relative concentrations of CH_3HgS^- in systems containing a low concentration of reduced sulfur species.

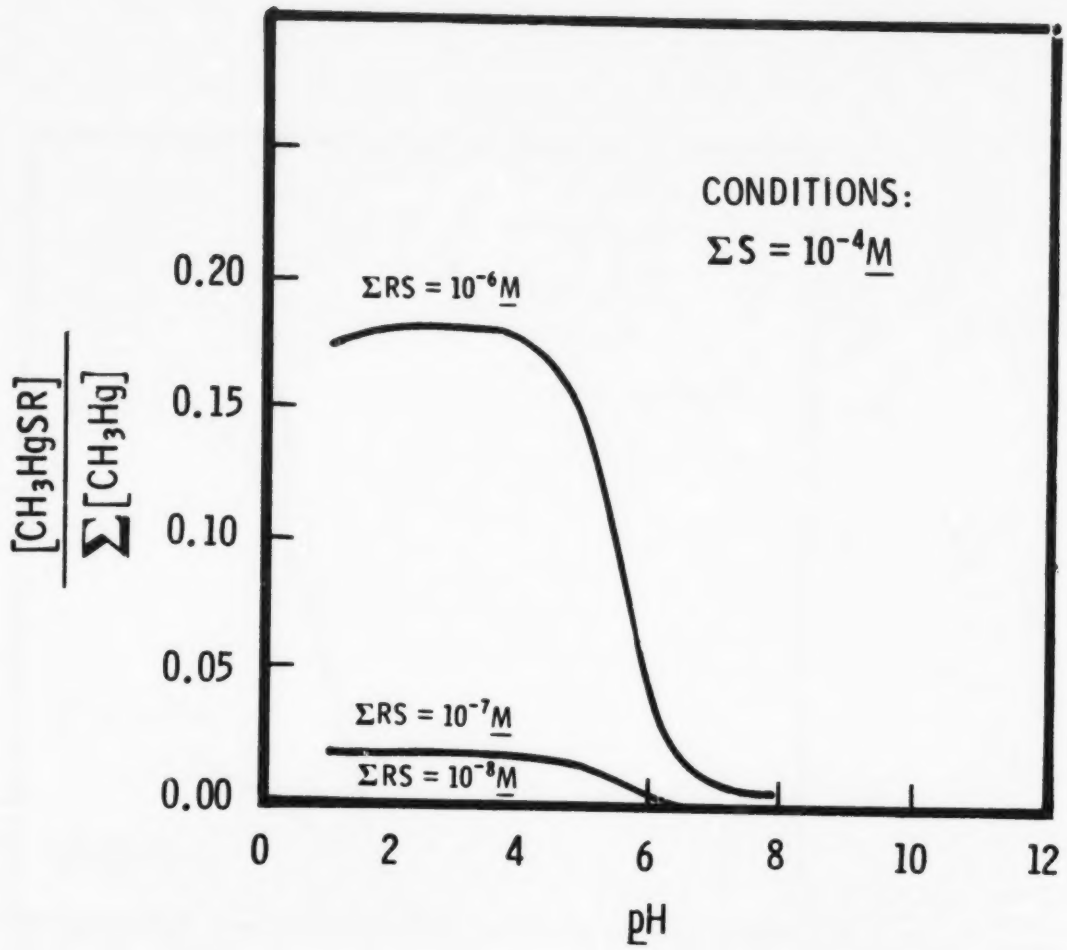

Figure A5. Relative concentrations of methylmercuric-thiol complexes in systems containing a high concentration of reduced sulfur species.

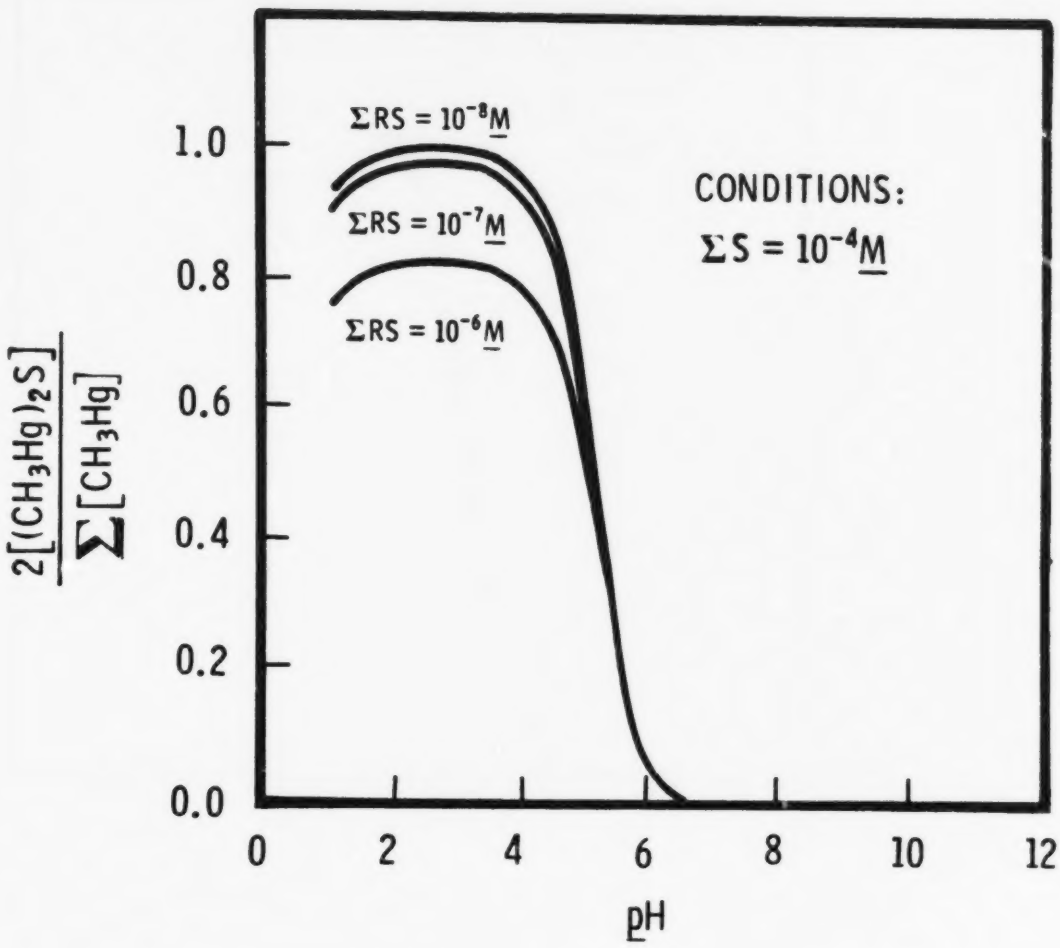

Figure A6. Relative concentrations of $(CH_3Hg)_2S$ in systems containing a high concentration of reduced sulfur species.

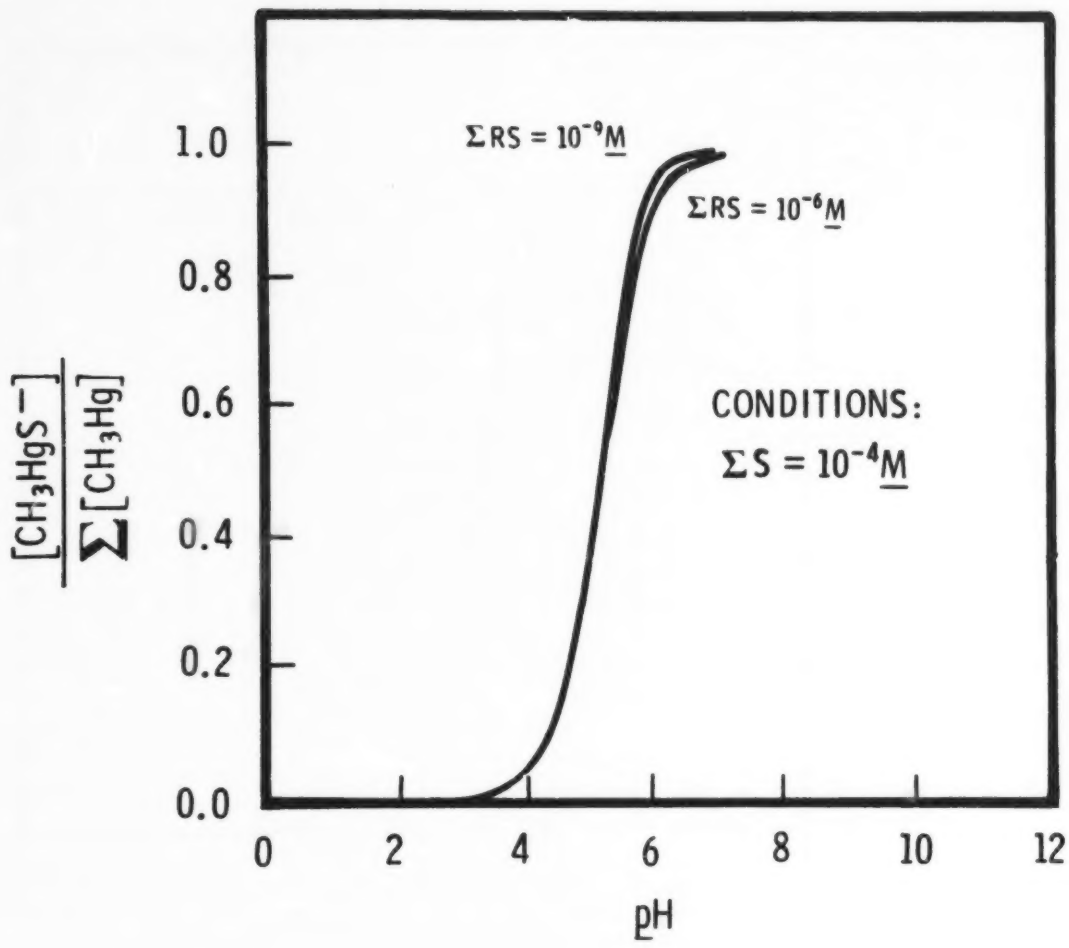

Figure A7. Relative concentrations of CH_3HgS^- in systems containing a high concentration of reduced sulfur species.

APPENDIX B

EQUILIBRIUM CONSTANTS FOR FORMATION, DISSOCIATION, AND HYDROLYSIS OF MERCURY SPECIES

Table B1. LOGARITHMS OF FORMATION CONSTANTS FOR Hg^{2+} COMPLEXES IN WATER AT 25° C

Ligand X[a]	$\text{Log } \frac{[HgX_2]}{[Hg^{2+}][X^-]^2}$ [b, c]
$-Cl^-$	13.2[c]
$-Br^-$	16.8[c]
$-I^-$	23.8[c]
$-OH^-$	21.7[c]
$-NH_3$	17.4[d]
$-NH_2R$ (Histidine)	21.2[e]
$-SR^-$ (Cysteine)	41.0[f]
$-SCN^-$	17.4[g]
$-CN^-$	34.7

[a] Sign to right denotes charge of unattached ligand.
[b] Taken from reference 15.
[c] Ionic strength = 0.5.
[d] Ionic strength = 2.
[e] Ionic strength = 0.15.
[f] Ionic strength = 1.
[g] Ionic strength = 0.1.

Table B2. LOGARITHMS OF FORMATION CONSTANTS FOR PHENYLMERCURIC COMPLEXES (C_6H_5HgX) IN H_2O, 25° C

Ligand X	Log $\frac{[C_6H_5HgX]}{[C_6H_5Hg^+][X^-]}$	Reference
$-OH^-$	9.89	16
$-OCOCH_3^-$	4.82	16
$-OCOCH_2CH_3^-$	4.51	16
$-SC_6H_5^-$	> 16	17

Table B3. LOGARITHMS OF FORMATION CONSTANTS FOR 18 METHYLMERCURIC COMPLEXES (CH_3HgX) IN WATER

Ligand X[a]	Log $\frac{[CH_3HgX]}{[CH_3Hg^+][X^-]}$ [a]	
$-F^-$	9.37	(9.5)
$-Cl^-$	5.25	(5.45)
$-Br^-$	6.62	(6.7)
$-I^-$	8.60	(8.7)
$-OH^-$	9.37	(9.5)
$-OC_6H_5^-$		(~ 6.5)
$-OCOCH_3^-$		(~ 3.6)
$-HPO_4^{2-}$	5.03	
$-HPO_3^{2-}$	4.67	
$-S^{2-}$	21.2	
$-SCH_2CH_2OH^-$	16.12	
$-SR^-$ (Cysteine)		(15.7)
$-SO_3^{2-}$	8.11	
$-S_2O_3^{2-}$	10.90	
$-SCN^-$		(6.1)
$-NH_3$	7.60	(8.4)
$-NH_2CH_2CH_2NH_2$	8.25	
$-CN^-$	14.2	

[a] Values in parentheses taken from reference 15 (ionic strength = 0.5, temp. 25° C); other values from reference 18 (ionic strength = 0.1, temp. 20° C).

Table B4. DEGREES OF DISSOCIATION OF 10 ORGANOMERCURY COMPOUNDS IN AQUEOUS SOLUTION AT 25° C

Compound	Degree of dissociation (%) at 10^{-4} M	10^{-7} M	10^{-10} M
$C_6H_5HgOCOCH_3$	32	> 99	> 99
C_6H_5HgSR	< 0.1	< 0.1	< 0.1
CH_3HgCl	21	98	> 99
CH_3HgBr	4.8	75	> 99
CH_3HgI	0.5	3.3	91
$CH_3HgOCOCH_3$	76	> 99	> 99
$CH_3HgHPO_4^-$	26	99	> 99
$CH_3HgNH_2R^+$	1.6	39	> 99
CH_3HgSR	< 0.1	< 0.1	< 0.1
CH_3HgS^-	< 0.1	< 0.1	< 0.1

Table B5. EQUILIBRIUM CONSTANTS FOR HYDROLYSIS OF MERCURIC, ALKYLMERCURIC, AND PHENYLMERCURIC IONS AT 25° C

Reaction	pK ($\log K^{-1}$)[a]	Reference
$Hg^{2+} + H_2O \rightleftarrows HgOH^+ + H^+$	3.70 ± 0.07	14
$HgOH^+ + H_2O \rightleftarrows Hg(OH)_2 + H^+$	2.60 ± 0.09	14
$Hg^{2+} + 2H_2O \rightleftarrows Hg(OH)_2 + 2H^+$	6.30 ± 0.05	14
$CH_3Hg^+ + H_2O \rightleftarrows CH_3HgOH + H^+$	4.50[b]	18
$C_2H_5Hg^+ + H_2O \rightleftarrows C_2H_5HgOH + H^+$	4.90[b]	16a
$C_6H_5Hg^+ + H_2O \rightleftarrows C_6H_5HgOH + H^+$	4.11[b]	16

[a] Ionic strength was 0.5 for all constants listed.
[b] Standard deviations not given.

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